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This Report summarizes the results of a research program focused on the distress of cementitious composites exposed to aggressive chemical substances found in nature. It presents a comprehensive summary of constituent physico-chemical processes such as diffusion with adsorption, kinetics of chemical reactions, stresses attributable to expansive reaction products and attendant microcracking.

Formulated analytical model was checked against available experimental data. The accuracy with which this data were duplicated is considered to be exemplary at this stage of the model development. (

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1. OBJECTIVE OF THE PROGRAM

This Report summarizes the two year research program focussed on the gradual loss of the mechanical strength and, eventually, integrity of concrete structures exposed to chemically aggressive substances commonly found in the environment. This program is a continuation of the research program on the micro-mechanics of concrete conducted previously by the principal investigator and his associates. Both of these programs were sponsored by the Civil Engineering Program, Directorate of Aerospace Sciences of the United States Air Force Office of Scientific Research.

The objective of these studies was primarily aimed on the better understanding of the complex physico-chemical phenomena leading to the deterioration of concrete reacting with the water-borne chemicals. The research described in this Report is obviously of basic nature since it represents an inquiry into the basic phenomena. Yet it also has undeniably practical implications as well. It appears obvious that this type of research can later serve as a basis for the improvements of the current design practices in order to enhance the economy and reliability of concrete structures such as runway pavements.

The nature of this problem and its scope, spanning over several scientific disciplines, requires parallel investigations of distinctly different, but inherently coupled, processes. Some of this processes are seldom, if ever, considered within the context of mechanics of concrete structures. In an effort to make this Report self-sufficient and, consequently, more useful for the reader the analytical modelling of chemical reactions and diffusion processes is in the sequel replicated in a sufficient detail. A list of references containing an even more comprehensive inquire into these processes was provided to help the interested reader feeling the need for a better understanding of the phenomena.

In discussing a sequence of phenomena as complex as the one reported herein it was often necessary to focus on a specific problem. A relative loss of generality was more than compensated by the depth of the insight gained through considerations of the selected case. The relative paucity of specific experimental data mandated a not entirely supported selection of a most likely scenario describing the process.

The general nature of the proposed model is micromechanical. The ultimate benefit arising from such an approach is that it enables establishment of rational relationships between the chemical composition of the hardened cement paste, morphology of the pore system, and defect distribution on one hand and the macroscopic (phenomenological) attributes of the specimens such as strength and durability on the other hand.

The considered problem of chemo-micro-mechanics of concrete is, obviously, too wide to be addressed in a comprehensive manner within a two year research program. Even though most of the considerations to be discussed in the sequel are of general validity (or will, at the very least, become a part of a more general analytical model) the studies summarized in this Report are focussed on:

- a specific double-decomposition chemical process leading to the formation of ettringite resulting from the exposure of the hardened mortar to waterborne magnesium sulphates,

- isothermal processes in order to reduce the number of thermodynamic variables and thermal diffusion,

- small to moderate pore pressures in order to be able to neglect the barrodiffusion and the influence of the pore pressure on the stress-strain relationship in the solid skeleton of the hardened cement paste, and

- the pre-critical processes with regard to the diffusion and mechanical response.

A generalization of these studies to the critical and post-critical phenomena, pressure driven flow through a porous media, and many other interesting phenomena is expected to become a part of subsequent studies.

2. INTRODUCTION

The general objective of this report is to relate the chemical composition of the concrete and the morphology of its microstructure to its chemo-mechanical response when exposed to chemically aggressive ambients. It is in this sense that the label chemo-micro-mechanics seems both descriptive and justified.

Naturally, this work is by no means the first one with such a lofty objective. For example, the chemically assisted fracture was studied by Rice (1978), Charles (1978), Cherepanov (1974), Fuller and Thomson (1979),

Thomson (1980), and many others on different levels of sophistication. A rather general discussion of degradation and chemomechanics was published by Aifantis (1980, 1981) who should also be credited with an initial continuum study of embrittlement (Colios and Aifantis, 1982). Many other papers with similar objective can be located in the existing literature. It is, nevertheless, felt that this Report is not only different from the similar efforts but that it also establishes a comprehensive framework for studies of an entire class of problems. Finally, this work has a practical aspect as well since it aspires to become ultimately a basis for a powerful tool in design of concrete structures.

Concrete is a complex composite material containing several active ingredients capable of reacting with the aggressive chemicals commonly found in the environment. These reactions are often deleterious for the integrity of concrete causing distress of structures and necessitating costly repairs and even costlier replacements.

As pointed out by Moavenzadeh (1971) the failure of a structure is not in itself a physical phenomenon but a condition or state of a complex process characterized by reduced reliability and inability of the structure to perform its functions. Consequently, in order to be able to predict the failure it is necessary to analyze the processes leading to the distress and establish criteria needed to distinguish the conditions portending the onset of failure. Thus, the analytical model must describe the evolution of variables representing physically identifiable measures of state and formulate conditions defining the limiting response of the material. For example, brittle failure of concrete occurs either as a result of a runaway growth of a single crack of preferential geometry or due to coalescence (cooperative action) of microcracks into a macrocrack. Hence, appropriate internal variables (Krajcinovic 1989) must be introduced into the analytical model to describe the manner in which the microcracks affect the mechanical response of the solid (compliance, diffusivity, etc.). For low to moderate crack densities a single internal variable (volume average) suffices. However, at the localization threshold the direct interaction becomes a dominant attribute and an appropriate internal length variable must be introduced in order to be able to predict the critical phenomena. At the threshold of the critical regime (distress) the evolution of the variable describing the state of damage (local loss of integrity) is rapidly accelerated. From the physical standpoint the process becomes non-local. Matnematically, the problem becomes strongly nonlinear and

in the case of the localization the governing differential equations cease to be elliptical causing further difficulties in analyses.

Analytical modeling of the environmental degradation of the hardened cement paste involves considerations of a complex, and not totally understood, physico-chemical process interrelating diffusion, adsorption, a double decomposition chemical reaction and evolution of damage (micro and macro-cracking). The complexity of these processes can be overwhelming since they in an essential manner depend on the chemical composition and microstructure of concrete. It is, therefore, not surprising that a reasonably comprehensive, and convincing, analytical modelling of this phenomenon is not as yet available. Moreover, the experimental evidence is often sketchy and directed towards conventional phenomenological modelling being of limited utility in micromechanical studies.

Among many interesting physico-chemical processes this paper focuses on the external sulphate attack on concrete. Contained in a wide range of industrial and agricultural effluents the magnesium sulphate proves to be a potent cause of degradation of a wide range of concrete structures such as pavements, culverts, bridges, hydraulic structures, etc. The internal sulphate attack (attributable to sulphates within the aggregates, see Ouyang, et al. 1988) will not be considered within this Report. Naturally, a reasonably straightforward modification of the proposed model should suffice to enable analyses of the internal attack as well.

The degradation of concrete as a result of exposure has been recognized by the ACI Committee 201 which in its "Guide to Durable Concrete" - ACI 201.2R-77 reflects on this problem in a rather cursory manner. In particular, the Committee suggests that in structures exposed to sulphate attack (seawater and groundwaters in western and norther U.S.) only the type V cement (less than 5% of C_3A or 20% of $C_4AF + 2C_3A$) be used. It also recommends classification of exposure into four classes with respect to the sulphate concentration. The Committee further recommends lower w/c ratios of 0.45 and advises against use of calcium chlorides (reducing sulphate resistance)

The sulphates can damage concrete also by a purely physical action by crystallization in the pores of concrete. The growing crystals (not reacting with the cement) can exert sufficient pressures to cause spalling of the outer layers of concrete (Reading 1975). Naturally, even the sulphate-resistant Type V cements are not impervious to this type of attack.

The objective of this study is to formulate a micro-mechanical theory modeling the dominant aspects of the underlying processes, blurring simultaneously the unnecessary details. The most important aspect of this study consists in providing a rational explanation of the experimentally measured trends. Specifically, the primary concern centers on providing a rational analytical model relating chemical composition of concrete and its morphology with the mechanical response. For example, it has been clearly established that the volumetric expansion of concrete depends not only on the concentration of sulphates and the time of exposure, but also on the composition of concrete and in particular on the mass fraction of the tricalcium aluminate. Even though the basic problem is very complex whenever possible and advisable an effort will be made to achieve the objective and retain the simplicity and tractability without compromising the rigor and physical insight into the underlying phenomena.

3. ANALYTICAL MODEL

Consider a hardened cement paste specimen saturated with clean, chemically inert, water, which is at time $t = 0$ immersed into a pool of water containing a known, and constant, concentration of magnesium sulphate MgSO4. The solute diffuses into the hardened cement paste specimen, triggers a sequence of complex chemical reactions and forms an expansive reaction product (ettringite). The attendant local stress concentrations in the material surrounding the inclusion in which the reaction took place, are often sufficient to cause microcracking of the hardened cement paste. The basic thermodynamic variables needed for the description of the process during which the mechanical strength of the concrete exposed to the magnesium sulphates (or some similar aggressive chemical substances) degrades, are:

- solute concentration $c(x,t)$ of the magnesium sulphate in the diffusing water,
- concentration of the adsorbent (gypsum) $c_g(x,t)$ on the adsorbate (wall of the pores of hardened cement paste),
- concentration of the reaction product (ettringite) $c_e(x,t)$ formed during the double decomposition reaction,
- elastic strain $\varepsilon(x,t)$ in the specimen, and

- mechanical history recording parameter (microcrack density) $\omega(x,t)$.

The rates of change of these thermodynamic variables are related through the kinetic equations such as those governing the rate of chemical reactions, diffusion equation, adsorption isotherms and damage evolution laws. The coefficients in these equations must be determined through careful experiments in conjunction with micromechanical considerations neither of which are, according to the consulted literature, commonly available.

Finally, it is necessary to determine the thermodynamic state of the material as defined by the two state parameters: diffusivity and mechanical compliance. In both cases the consideration was at this point restricted to the pre-critical regime. Nevertheless, the derivation of micromechanically rigorous expressions for the diffusivity and compliance tensors requires consideration of the internal damage, i.e. presence of a large number of microcracks distributed over a large part of the affected volume. In a subsequent research program, to be proposed shortly, these investigations will be extended to the post-critical regimes considering the propagation of the percolation and fragmentation fronts through the hardened cement paste and the behavior of material swept by these two fronts.

The processes of diffusion, adsorption, chemical reaction and microcracking are inherently coupled. For example, the extent of the chemical reaction obviously depends on the transport of magnesium sulphates through the hardened cement paste (diffusion or flow through the porous media). The rate of transport of aggressive chemical substances is enhanced by microcracking which opens new, wider and more direct paths for the percolating fluid. However, the microcrack nucleation and evolution is directly attributable to the formation of ettringite crystals which are in turn the products of the chemical reactions.

Many other coupling effects such as influence of the macro-stress sign (compression or tension) on the crack width and, therefore, diffusivity, influence of the pore pressure on the stress-strain relationship, thermal effects associated with the exothermic reactions, etc. will at this point be considered as being of secondary importance and, consequently, ignored.

In summary, the analytical model will consist of several partial and ordinary differential equations defining the salient aspects of the problem such as the rate of chemical reactions, diffusion with adsorption and the mechanical equilibrium. These equations will be formulated in this Report sequentially and

8

almost independent of each other. The Report will also contain a description of simplifications introduced to enhance the tractability and brief discussions of trends in future development of the proposed model. Naturally, the accuracy and predictive ability of the model will be tested against the available experimental data. The main emphasis of this comparison will be in relating the macro-response of the mortar specimen to its micro-structure and chemical composition.

The flow chart shown in Fig. 1 represents the general structure of the model to be developed in detail in the subsequent sections of this study.
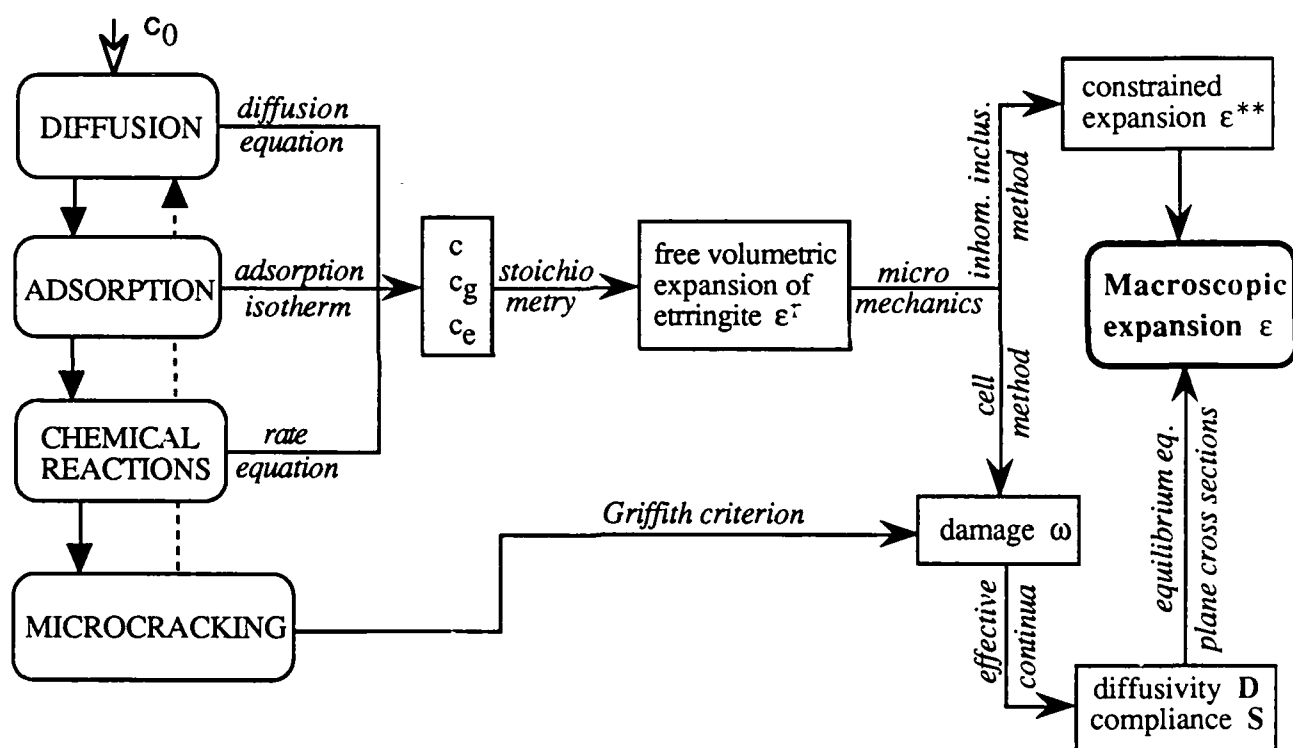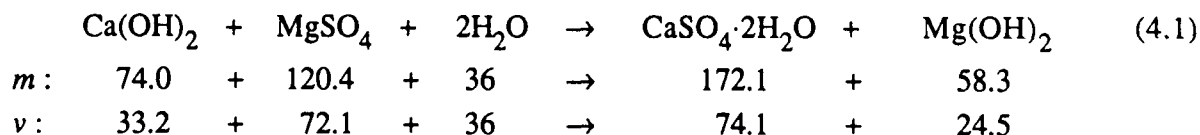
Fig. 1. Schematic structure of the proposed model for the sulphate corrosion induced degradation of concrete
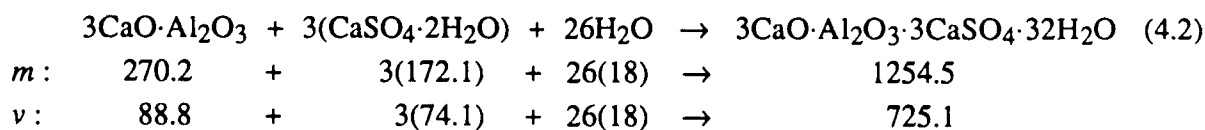
4. CHEMICAL REACTION

A review of the existing literature reveals a reasonable concensus with regard to the main points of the so-called double decomposition reaction leading to the formation of ettringite during the exposure of the hardened cement paste to the water borne sulphates. However, the exact details of these reactions are still a matter of debate and disagreement. In this paper the so-called Hansen's model (1968) will be taken as the starting point. The proposed model can readily accommodate other decomposition reactions which can be found in the literature, without changes in its basic structure.

Recently reported experiments (Odler and Gassser 1988, Moukwa 1990) confirm the essential nature of the micromechanical changes associated with $MgSO_4$ attack on the cement paste. Careful measurements indicate a substantial reduction of the total porosity (10% - 20%, Moukwa 1990) resulting from the expansion products filling the pores. The expansion develops rather slowly since the pore space suffices to accommodate the ettringite crystals initially. After protracted exposure (in excess of half a year) the internal fracture (damage) becomes apparent since the remaining pore space is insufficient to provide enough room for the expanding needle-like ettringite crystals. According to Moukwa (1990) the "examination of fractured surfaces in the scanning electron microscope indicated that the formation of such reaction products probably was the main cause of deterioration."

According to Hansen (1968) the double decomposition reaction taking place in the hardened cement paste inundated by a solution of magnesium sulphate can be summarized by the following equations

$$Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2 \quad (4.1)$$

m:	74.0	+	120.4	+	36	$\rightarrow$	172.1	+	58.3
v:	33.2	+	72.1	+	36	$\rightarrow$	74.1	+	24.5

and

$$3CaO \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (4.2)$$

m:	270.2	+	3(172.1)	+	26(18)	$\rightarrow$	1254.5
v:	88.8	+	3(74.1)	+	26(18)	$\rightarrow$	725.1

where the molar masses m (g/mol) and molar volumes v (cm^3) are listed below each chemical substance taking part in the reaction (see also Appendix A).

The first of the two reactions (4.1) is a through-solution reaction. The reaction products (gypsum and magnesium hydroxide) are readily accommodated by the porosity of the mortar. Simple computations clearly indicate "that concrete cannot be caused to expand and crack by the simple mechanism of filling pores with solids by a through-solution process" (Hansen 1968, page 32).

The second reaction (4.2), involving tricalcium aluminate, newly formed gypsum and water needed to form the ettringite, is often assumed to be of the solid-liquid or topochemical kind. In this case, "the space available locally at the surface is not big enough to accommodate the newly formed crystal" (Soroka, 1979, page 153). The expansion of the newly formed ettringite crystal may, therefore, cause large local tensile stresses sufficient to induce cracking of the hardened cement paste in the vicinity of the pores.

The Hansen's model (4.1 - 2) is not the only one to be found in the literature. Mather (1968) proposes two alternatives: a single decomposition and a double decomposition (somewhat similar to Hansen's) reaction. Biczok (1972) proposes a change in the reaction (4.2) and recognizes two alternatives of that reaction for pH below or above 12.5. Mindess (1981) also agrees with the first of the two reactions but allows for transformation of the ettringite to monosulphate in the case when all sulphates are consumed before the tricalcium-aluminates are completely hydrated. According to Lea (1970) and Soroka (1979) the second of the two reactions involves C_4AH_{19}.

Naturally, it is very difficult to determine which one of these reactions is typical of the considered case. Moreover, on the technical scale the ASTM C1012 Standard recommends the aqueous magnesium sulphate ($MgSO_4 \cdot 7H_2O$) to be used in the expansion tests (instead of $MgSO_4$) The listed ASTM Code also specifies the range of the pH factor between six and eight.

4.1. Stoichiometric analysis

The masses of the formed gypsum and ettringite and the masses of the substances "consumed" in the course of the chemical reactions (4.1) and (4.2) can be determined using conventional stoichiometric analyses.

Denote by:

$c(x,t) \rightarrow$ concentration of magnesium sulphate in the water

$\phi \quad \rightarrow$ accessible porosity of the hardened cement paste

$m \quad \rightarrow$ molar mass (g/mol)

$M \quad \rightarrow$ total mass of a substance in volume $V = 1$ m^3.

$v \quad \rightarrow$ molar volume (cm^3).

$\gamma \quad \rightarrow$ mass densities

and use the following subscripts:

s for   magnesium sulphate

cm for   cement

c for   calcium hydroxide

a for   tricalcium aluminate

g for   gypsum

e for   ettringite.

Superscripts c and f stand for masses consumed and formed in the course of a given chemical reaction. The relevant data for the molar masses and volumes of all substances involved in reactions (4.1) and (4.2) are assembled and tabulated in the Appendix A to this Report.

Consider now the chemical reaction (4.1). The mass of the gypsum formed during this reaction may be controlled either by the supply of sulphates (if the ratio $M_s/M_c < m_s/m_c = 1.63$) or by the available mass of calcium hydroxide (if $M_s/M_c > 1.63$). Rather elementary stoichiometric analyses suffice to determine the mass of the newly formed gypsum

$$M_g^f = min \, [(m_g / m_s)\phi \, c\gamma_{sol}V \, , \, (m_g / m_c)f_c' M_{cm}] \tag{4.3}$$

while the mass of the calcium hydroxide consumed in the course of the reaction (4.1) is

$$M_c^c = min \, [(m_c / m_s)\phi \, c\gamma_{sol} \, V \, , \, f_c' M_{cm}] \tag{4.4}$$

In the two above equations f_c' denotes the mass fraction of calcium hydroxide with respect to the mass of cement, $M_s = c \, \phi \, \gamma_{sol} \, V$ is the mass of sulphates with γ_{sol} denoting the density of magnesium sulphate solution. The mass fraction of the

calcium hydroxide f'_c can be readily determined by a similar stoichiometric analysis of the hydration reaction of the C_3S and C_2S. Since the experiments indicate no dependence of the volumetric expansion on the available mass of the calcium hydroxide this alternative can be, at the moment, safely discarded.

The mass of the consumed tricalcium aluminate during the second (topo-chemical) reaction (4.2) can be then determined to be

$$M_a^c = min \, [(m_a / 3m_g) \, M_g^f \; ; \; f'_a M_{cm}] \tag{4.5}$$

depending again on whether the reaction is controlled by the supply of gypsum $(M_g / M_a < 1.91)$ formed during the preceding through-solution reaction, or the available mass of the tricalcium aluminate (when the inequality sign is reversed). In (4.5) f'_a denotes the mass fraction of tricalcium aluminate calculated with respect to the mass of cement.

In conjunction with (4.3) the expression (4.5) can be rewritten in the form

$$M_a^c = min \, [(m_a / 3m_s)\phi \, c \, \gamma_{sol}V \; ; \; (m_a / 3m_c) f'_c M_{cm} \; ; \; f'_a M_{cm}] \tag{4.5$_1$}$$

Finally, the mass of the ettringite formed in the course of the topochemical re-action (4.2) is

$$M_e^f = (m_e / m_a) \, M_a^c = min \, [(m_e / 3m_s)\phi \, c\gamma_{sol}V \; ; \; (m_e / 3m_c) f'_c M_{cm} \; ; \; (m_e / m_a) f'_a M_{cm}] \tag{4.6}$$

Consequently, the mass of the ettringite formed is controlled by: (a) the mass of the available sulphates, (b) available calcium hydroxide or (c) by the tricalcium aluminate contained within the hardened cement paste. While theoretically rigorous, these expressions contain several uncertainties which may affect their accuracy. For example, the accessible porosity cannot be easily derived. Water can be stored in concrete in large bubbles, pores of different radii (ranging from 130 to 500 nm, see Bazant, et al. 1988), and intragel space. The accessibility of these passages depend on the complex morphology and connectivity of the pore space and can vary within rather wide limits from case to case. Secondly, some ettringite is already present (and some tricalcium aluminate already consumed) in

the cement paste during hardening as a result of the addition of gypsum needed to avoid rapid setting.

Knowing the masses "formed" and "consumed" during the reactions (4.1) and (4.2), and the densities of these substances, it is rather straightforward to determine the free volumetric strain attributable to the double decomposition reaction. The computations indicate that the mass of the ettringite formed will almost never depend on the calcium hydroxide available in the cement paste. Neglecting that possibility, the volumetric expansion computed from the stoichiometric (mass balance) analyses can be written as

$$e^V = \Delta V / V = (M_e^f / \gamma_e) - [(M_c^c / \gamma_c) + (M_a^c / \gamma_a)] \tag{4.7}$$

From the expressions derived above the free volumetric expansion of the reaction products can be written in a simple form as

$$e^V = 3\beta_1 c_e \quad \text{for} \quad c_e < c^s \quad \text{or} \quad e^V = 3\beta_1 c^s = const \quad \text{for} \quad c_e \geq c^s \tag{4.8}$$

where β_1 denotes the coefficient of linear expansion of the ettringite crystal.

The first of the two expressions (4.8) corresponds typically to the beginning of the process during which the reaction depends on the available sulphates. At some point defined by

$$c_e = c^s = (f_a' m_e M_{cm}) / (\phi \gamma_{sol} V m_a) \tag{4.9}$$

the entire supply of the tricalcium aluminate available in the hardened cement paste is exhausted and the reaction is terminated.

The coefficient β_1 is obtained comparing (4.7) and (4.8) in conjuction with (4.9)

$$\beta_1 = \frac{\left(M_e^f / \gamma_e\right) - \left[\left(M_c^c / \gamma_c\right) + \left(M_a^c / \gamma_a\right)\right]}{3 f_a' m_e M_{cm} / \phi \gamma_{sol} V m_a} \tag{4.10}$$

However, the already discussed uncertainties will affect the accuracy of these calculations.

The expression (4.10) can be further recast into a more convenient form for computations using $(4.8)_2$ and (4.9)

$$\beta_1 = \frac{e^V(c_e = c^s)}{3c^s} = \frac{\phi \gamma_{sol}}{3m_e} \left(\frac{m_e}{\gamma_e} - \frac{3m_c}{\gamma_c} - \frac{m_a}{\gamma_a}\right) \tag{4.10}$$

Even though the rigorous determination of the exact value of the coefficient of linear expansion β_1 (see also, Sih, et al. 1986) might not fall within the realm of realistic expectations in the case of a material with a random morphology of microstructure, the fact remains that the performed stoichiometric analysis clearly indicates the major experimentally determined trends in the deformation process. In other words, the expressions (4.8) reflect the fact that the extent of expansion is in the short term controlled by the concentration of the diffusing sulphates. In the long term (i.e. protracted exposure) the volumetric expansion depends only on the chemical composition of the cement (i.e. the mass fraction of the tricalcium aluminate present in the hardened cement paste). The limit between the short and long term exposure is defined by the expression (4.8) in conjunction with the diffusion equation (defining the time dependence of the solute at a particular location).

4.2. Kinetics of ettringite formation

Even a superficial perusal of the extensive literature concerning the formation of ettringite reveals a profound lack of consensus among the cement chemists as to the actual type of the underlying chemical reaction (4.1-2). Schwiete, et al. (1966), Hansen (1968), Soroka (1979) claim that ettringite is formed by a solid-state (topochemical) mechanism at the surface of anhydrous C_3A crystals. Chatterji (1968), and Mehta (1976, 1983) supported by scanning electron microscopy observations of the ettringite morphology hypothesized that ettringite is formed by a through-solution mechanism. Other authors (Biczok 1972, Ogawa and Roy 1982) Maintain that ettringite may be formed either by a solid-state conversion or a through-solution reaction, or both. If both mechanisms are present the topochemically formed ettringite is believed to cause microcracking. During the crystallization of ettringite from the diffusing solution

the crystals are likely to gradually fill (plug) the pores and initially even improve the strength of the cement paste (Biczok 1972).

Naturally, the chemical reaction irrespective of type is not an instantaneous process. In the considered case the situation is somewhat more complicated by the fact that the basic reaction (4.1-2) is heterogeneous, i.e. involves reactants in more than one phase. Before the substances can react they must migrate at least to the solid-liquid interface. Therefore, in addition to the rate of chemical reaction, certain physical factors affect the rate of mass transfer between phases, and the overall rate of the heterogeneous reaction. According to Walas (1959) these factors are:

- amount of the available interfacial surface to which the rate may be proportional (surface-controlled mechanism)

- rate at which the liquid diffuses to and through the interface film (diffusion-controlled mechanism)

- rate of the backward diffusion (important in reversible reactions only)

Consequently, a complete formulation of the rate equation for a heterogeneous reaction should involve the rate equations governing both the mass transport and the chemical reaction itself.

Several studies have addressed in the past the kinetics of ettringite formation. A majority of these studies support the view that this process is controlled by the diffusion of the sulphate ions to the anhydrous C_3A particles (e.g. Tenoutasse 1968, Mori and Minegishi 1968, Plowman and Cabrera 1984, Pommersheim and Chang 1986, 1988, Brown and LaCroix 1989).

Having in mind the already mentioned controversy, and in the same time trying to keep the proposed model tractable, it seems reasonable to introduce the following simplifications:

- diffusion equations for the sulphate ions contained both in $MgSO_4$ and in newly formed $CaSO_4 \cdot 2H_2O$ will be cast into a single governing diffusion equation. The diffusion will be considered as a time limiting step in the process of ettringite formation,

- the through-solution reaction (4.1) is assumed to be instantaneous as compared to (4.2), and its rate will not limit the overall rate,

- the reaction (4.2) (considered to be of the solid-state type) will affect the overall rate but not as much as the diffusion process. The kinetic equation for (4.2) will, nonetheless, be included in the governing equations of the model.

In summary, it seems reasonable to consider the two processes simultaneously as a diffusion equation with a sink (reflecting "loss" of sulphates reacting with the active constituents of the cement paste). Moreover, there seems to be no practical (or experimental) way to separate the diffusion of the sulphates through the pores from the diffusion of gypsum through the cement paste in search for C₃A. Thus, these two diffusion processes are simply joined into a single one.

The diffusion will be considered in detail in Section 5 of this Report. The remainder of this Section will be focused on the formulation of the rate equation for the topochemical reaction (4.2).

In general the rate at which the molar concentrations change during a chemical reaction of the type ($pA + qB \rightarrow lL$) is defined by an ordinary differential equation of the form (Walas 1959, Dawson 1973, etc.)

$$\frac{dx}{dt} = k(a - \frac{p}{l}x)^{\alpha}(b - \frac{q}{l}x)^{\beta}$$

(4.11)

where: x denotes an increase in the molar concentration of the reaction product L, t is time, a, b are the initial molar concentrations of the reactants A, B; the exponents α and β are small integers or fractions. The reaction orders α and β are unity only in the case of simplest forward reactions. In the case of catalitic, crosscatalitic, autocatalitic or reverse equations the order of the reaction changes. The coefficients p/l and q/l are determined by the stoichiometry of the reaction. In (4.11) k is the rate constant of the process (depending on the temperature and pressure) defining the fractions of all collisions that are reactive. Obviously, the dimension of this constant depends on the overall reaction order $(\alpha + \beta)$. It should be stressed here that there is no generally useful theory that predicts the rate laws. The rate law must be found from suitably designed experiments (Kotz and Purcell 1987, Mijovic and Ott 1989). According to the consulted literature such data do not seem to be available for the considered double decomposition reaction (4.1-2). Therefore, as the simplest alternative, it will be assumed that the topochemical reaction (4.2) proceeds according to a second-order rate law:

$$\frac{dc_e}{dt} = k(c_g^0 - 3c_e)(c_a^0 - c_e)$$

(4.12)

where c_e is the actual molar concentration of ettringite, c_g^0, c_a^0 are the initial molar concentrations of gypsum and tricalcium aluminate. The equation (4.12) simply states that the rate of ettringite formation is linearly proportional to the available concentrations of gypsum and tricalcium aluminate.

The rate equation (4.12) will be somewhat modified in the Chapter 7 where molar concentrations of the substances will be replaced by their mass percentages with respect to some reference mass M. The reason behind this conversion is the solid-liquid character of the reaction (4.2). In this case the conventional reference volume (1L of solution) seems to be inappropriate. Conceptually, once the data concerning the order of the rate laws for (4.1-2) become available the proposed model can be readily adjusted.

Chemical equilibrium ("attractor" state) is reached when either all of the tricalcium aluminate is exhausted or when all of the adsorbed gypsum is spent. The latter case will typically occur only if the diffusion process is terminated through the interruption in the supply of the magnesium sulphate. In both cases the termination of the reaction signals the end of the expansion and, consequently, the cessation of the deformation process (Mather 1968).

It is important to point out that the formation of an ettringite crystal per se implies that it exerts large pressures on the the surrounding matrix. As argued by Hansen (1968) only some of the crystals growing in places restricting their free expansion (via constrictions in the pore size) will exert pressures on the hardened cement paste sufficient in magnitude to nucleate and subsequently propagate a crack.

5. DIFFUSION WITH ADSORPTION

5.1. Diffusion Equation

As already mentioned the extent of the considered chemical reaction strongly depends on the availability of the magnesium sulphates. The magnesium sulphate is brought into contact with the cement paste in form of a solute contained in the water penetrating through the pores of the hardened cement paste. In general, the conduction of water may be ascribed to many causes. However, the pressure and concentration gradients are generally considered to be the two most frequent

generalized forces driving the water through the solid. In this Report it will be assumed that the water is driven through the pores of the hardened cement paste by the gradient of the concentration $s(\mathbf{x}, t) = \mathbf{grad}\ c(\mathbf{x}, t)$ of the solute in the water.

Even though the derivation of the diffusion-adsorption equation is available in the literature a short precis of the underlying theory seems to be in order for the sake of completeness of this Report. Consider a problem of a concrete slab saturated with inert water. At time $t = 0$ at least one of the external surfaces of the slab is exposed to water with some concentration c of a chemically aggressive solute. In the case when the pressure gradients are small it can be assumed that the mixing (process of gradual homogenization of two fluids) occurs via diffusion, i.e. by the molecular mass transport of solute from the external fluid to one contained within the accessible pores of the slab. Naturally, this process is irreversible and, consequently, energy must be dissipated during the diffusive mass transport.

The conservation of mass equation, in conjunction with the equation of continuity, leads to the well known partial differential equation governing the process of diffusion

$$\rho\left(\frac{\partial c}{\partial t} + \mathbf{v}\nabla c\right) = -div\ \mathbf{i} + q(c, t)$$

(5.1)

In (5.1) $c(x,t)$ is the concentration of the solute, $\mathbf{v}(x,t)$ the velocity of convective flow, ρ the fluid density and $q(c, t)$ the source term reflecting the change in the concentration attributable to the adsorption of solute on the adsorbant (hardened cement paste). The thermodynamic current (flux) density $\mathbf{i}(c,t)$ represents the mass of solute diffusing through the unit surface during a unit of time.

The internal (Gibbs') energy density (Glansdorf and Prigogine 1971) is given by

$$de = Tds + pdV - \sum_i \mu_i\, dn_i$$

(5.2)

where $T,\ s,\ p$ and V are the absolute temperature, entropy, pressure and volume, respectively. Additionally, μ_i and n_i are the chemical potential and

the number of particles (moles) of the i-th substance within volume V. From the conservation of mass

$$\sum n_i m_i = 1 \tag{5.3}$$

where m_i is the mass of the i-th particle. Thus,

$$\sum m_i dn_i = 0 \tag{5.4}$$

Expressing, furthermore, the concentration in terms of the total mass of particles

$$c = n_1 m_1 \tag{5.5}$$

the expression (5.2) for the internal energy density can be rewritten in form

$$de = Tds + pdV - \mu dc \tag{5.6}$$

where (in the case of mixing of only two substances)

$$\mu = \frac{\mu_1}{m_1} - \frac{\mu_2}{m_2} \tag{5.7}$$

is the generalized chemical potential.

The generalized chemical potential μ is the function of the concentration c, temperature T and pressure p. Thus, its gradient can always be written as

$$\nabla \mu = \left(\frac{\partial \mu}{\partial c} \right)_{p,T} \nabla c + \left(\frac{\partial \mu}{\partial T} \right)_{p,c} \nabla T + \left(\frac{\partial \mu}{\partial p} \right)_{c,T} \nabla p \tag{5.8}$$

where the subscripts to the right of the parentheses denote variables held fixed.

Assuming further the process to be thermodynamically stable and the field gradients small, the current density $\mathbf{i}$ is (Landau and Lifshitz 1988) a linear function of the gradients of the chemical potential and temperature

$$\mathbf{i} = -\alpha \nabla \mu - \beta \nabla T \tag{5.9}$$

where α and β are some constants.

Substitution of (5.7) into (5.8) leads after some obvious manipulations to

$$\mathbf{i} = -\rho D \mathbf{I} = -\rho D \left(\nabla c + \frac{k_T}{T} \nabla T + \frac{k_p}{p} \nabla p \right) \tag{5.10}$$

where $\mathbf{I}$ is the field intensity and

$$D = \frac{\alpha}{\rho} \left(\frac{\partial \mu}{\partial c} \right)_{p,T} \quad , \quad \frac{\rho D}{T} k_T = \alpha \left(\frac{\partial \mu}{\partial T} \right)_{c,p} + p \quad , \quad \frac{\rho D}{\alpha p} k_p = \left(\frac{\partial V}{\partial c} \right)_{p,T} \tag{5.11}$$

the diffusivity parameters.

In a general case of viscous fluids the situation is much more complex and requires careful modifications of above expressions in the spirit of the diffusion model suggested by Aifantis (1980). Restricting present discussion to non-viscous fluids the governing equation can be obtained substituting (5.10) into (5.1)

$$\rho \left(\frac{\partial c}{\partial t} + \mathbf{v} \nabla c \right) = div \left[\rho D \left(\nabla c + \frac{k_T}{T} \nabla T + \frac{k_p}{p} \nabla p \right) \right] + q(c,T) \tag{5.12}$$

In the present case the temperature T is considered to be a known function of time and space. Generally, this might not be the case and an additional partial differential equation defining time rate of change of entropy as a function of thermal flux (depending on T and μ) must be added (Landau and Lifshitz 1988) to allow for a simultaneous determination of T and c. At this point, however, T will be regarded as being known. Additional simplifications will be introduced since in its most general form equation (5.1) does not lend itself well to analyses of the type considered appropriate for the initial phase of this research project.

On the basis of experimental observations it seems appropriate to assume that the process is slow and that the mass transport by conduction (i.e. diffusion) vastly exceeds that by convection. In other words, it will be assumed that the second term on the left hand side of (5.12) can be neglected.

Furthermore, the solution concentration $c(x, t)$ is, in the considered case, of the order of several percent. Noting that the coefficients of thermal and

barrodiffusion k_T and k_p must vanish when c approaches zero (since no diffusion takes place at vanishing concentration) the second and third term within the brackets on the right hand side of (5.12) can be neglected as well.

The source term is typically represented in terms of the time rate of change of the amount of adsorbate on the adsorbent (hardened cement paste) per unit volume. At a given temperature and pressure a definite relation is found to exist between the number of molecules adsorbed and the concentration of the solute. This relation, defined by isotherms, is measured experimentally for each specific process under controlled conditions. When only few sites on the surface of the pore are occupied the so-called Henry's law (Compton 1989) applies and the loss of the sulphate concentration attributable to adsorption is

$$c^A = k_1 c \tag{5.13}$$

where k_1 (kinetic rate constant of the process) is a parameter of the system. In some applications similar to the presently considered one (Banks and Jerasate 1964) this linear law was shown to be quite useful. In other cases the linear law (5.13) leads to a less than satisfactory fit of the experimental data necessitating application of more complex and nonlinear isotherms (Langmuir, Freundlich, etc.). In view of an almost total lack of experimental data it seems advisable to use the simplest expression (5.13) available. Naturally, the expression (5.13) neglects the hysteresis in the adsorption-desorption cycle which is, strictly speaking, appropriate only when the pores are perfect cylin-ders and in absence of the residual liquid films covering the pore walls.

On the basis of (5.13) the source term can then be written as

$$q(c,T,p) = -\left(1 / \phi\right) \frac{\partial c^A}{\partial t} = -\left(k_1 / \phi\right)\frac{\partial c}{\partial t} \tag{5.14}$$

With all mentioned simplifications the final form of the diffusion equation (5.12) reads

$$\frac{\partial c}{\partial t} = div\left[\mathbf{D}^e\left(\nabla c\right)\right] \tag{5.15}$$

where

$$\mathbf{D}^e = \mathbf{D}\left[1 + (k_1/\phi)\right]^{-1} \qquad (5.16)$$

is the effective diffusivity accounting for the adsorption in the sense of approximations (5.13) and (5.14). In general, the diffusivity is neither isotropic nor homogeneous. These two points will, however, be discussed in the sequel.

In the case of constant diffusivity and infinite half-space the Fickian diffusion equation (5.14) admits a closed form solution in the form of error functions (Carslaw and Jaeger 1959, Greenkorn 1983, Landau and Lifshitz 1988, etc.). For a finite slab the solution can be derived in form of a rapidly converging infinite trigonometric series (Carslaw and Jaeger 1959). In the case of arbitrary geometry and/or variable diffusivity the solution can be reached only through application of approximate (such as various types of the method of weighted residuals, see for example, Finlayson 1972) or purely numerical methods. Since the diffusivity in the considered case involves adsorption and microcracking, neither of which is homogeneous, a closed form analytical solution seems to be out of reach.

5.2 Diffusivity

The diffusivity $\mathbf{D}$ is a structural parameter with a strong dependence on the tortuosity of the fluid path through the solid (Dullien 1979). In a virgin hardened cement paste the diffusivity depends on the pore structure, i.e. the distribution (and connectivity) of pores $\phi(r)$ of various widths. Assuming the pores to be perfectly random with respect to their orientation and width the virgin (undamaged) hardened cement paste may be considered to be of isotropic diffusivity. For the present purposes it will be assumed that the accessible porosity ϕ and isotropic diffusivity $\mathbf{D}^o$ characterizing diffusion in the virgin hardened cement paste are known.

As the microcracks within the specimen nucleate and grow the tortuosity of the fluid path decreases and the diffusivity increases. This problem was discussed by many authors in the past on many levels of rigor and sophistication (Barenblatt, et al. 1960, Salganik 1974, Dienes 1982, Englman, et al. 1983, Wilke, et al. 1985, Bazant, et al. 1987, Babushkin, et al. 1987, Gueguen and Dienes 1989, etc.).

The purely continuum models, popular among analysts because of their computational efficiency, ignore the microscopic nature of the mixing process. In general, these models are based on the volume averages of the involved field quantities and variables and are, therefore, applicable in the initial stages of the process away from the critical phenomena (such as percolation threshold). Even in these stages of the process, i.e. when the microcrack density within the solid is of moderate levels, it is often argued that the nature of the problem necessitates application of statistical models (see Torelli and Scheidegger, 1972, etc.) based on the studies of a random network of capillaries. This is especially important when the distribution of the capillary sizes is not isotropic.

Even newer studies of the so-called percolation problems fully support the stochastic character of the problem. Moreover, these studies (see, for example, Stauffer 1985) indicate existence of the scale effect (which is of great interest in the process of interpreting the experimental results) and a radical change in flow patterns and diffusivity in the neighborhood of the critical regime (percolation threshold). These studies may, therefore, become pertinent during investigations of the localized phenomena characterized by the emergence of large cracks. This work will, hopefully, be completed in the proposed continuation of this research program.

The strategy adopted by Salganik (1974), developed within the framework of the effective continua theories, appears to be most promising and suitable for the present purposes. Consider a volume V of an isotropic matrix of diffusivity D^0 containing an isotropic inclusion of diffusivity $\mathbf{D}^*$. The effective flow density through the volume is then given by a vector equation

$$j_m = (1 - f)j_m^0 + f j_m^*$$ (5.17)

where $f = V^* / V$ is the volume fraction of the inclusion. The superscripts (0) and (*) refer to the matrix and the inclusion. The flow densities (currents) are

$$j_m = D_{mn} s_n \qquad j_m^* = D_{mn}^* s_n^* \qquad j_m^0 = D_{mn}^0 s_n^0$$ (5.18)

where $s_m = \left(\partial c / \partial x_m\right)$ is the driving force (concentration gradient).

Introducing the mapping tensor A_{mn} it is possible to write the concentration gradient within the inclusion as a function of the effective concentration gradient in form

$$\int_{V^I} s_n^* \, dV = V^I A_{nm} s_m \tag{5.19}$$

where V^I is the inclusion volume.

In the present case the interest is centered on the determination of the average diffusivity of the hardened cement paste containing many spheroidal inclusions. Moreover, this average diffusivity is related to some effective macro continuum which in a smoothed manner relates to the actual inhomogeneous microstructure. In order to accomplish the transition between the effective macrocontinuum and the inhomogeneous actual solid containing a large number of inclusions of different sizes, shapes and orientations it becomes necessary to introduce the concept of a representative volume element. A representative volume element must be large enough to contain a statistically valid sample of inhomogeneities. Selected in such a manner it enables transiti-on between the two scales mapping the actual solid on a material point of the effective continuum.

For a dilute concentration of spheroidal inclusions the expression (5.19) remains valid with a proviso that the integral on the left hand side of (5.19) is taken over all inclusions contained within the representative volume element of volume V circumscribed about the material point in which the diffusivity is sought. Since the number of inclusions within the representative volume is by definition large the sums can be recast into integrals taken over all sizes and orientations of these inclusions.

Substituting (5.18) and (5.19) into (5.17) it becomes possible to derive the expression for the effective diffusivity in form

$$D_{mn} = D_{mn}^0 + \left(D_{mk}^* - D_{mk}^0\right) \int_Y A_{kn} B(Y) \, dY \tag{5.20}$$

Expression (5.20) is subject to the normalizing condition

$$\int_Y B(Y)\, dY = N \tag{5.21}$$

In (5.21) N is the number of inclusions contained within the volume V. The function $B(Y)$ contains the probability density distributions of inclusion sizes and orientations within the solid element dY.

The form of the expression (5.20) for the diffusivty implies introduction of the assumptions common to the so-called self-consistent methods (Mura 1982, Kunin 1983, Krajcinovic and Sumarac 1987, etc.). This type of methods is based on the premise that the direct interaction between inclusions (and/or cracks) is negligible and that the external fields of every inclusion do not significantly differ from the respective far-fields. Consequently, the valid, of the expression (5.20) is, strictly speaking, limited to the low-to-modest inclusion concentration. It is notable, that the concentration gradient s within the inclusion is homogeneous in the case of homogeneous far field fluxes (Landau, et al. 1988).

Assuming that both the matrix and the inclusion are isotropic

$$D^0_{mn} = D^0\, \delta_{mn} \qquad \text{and} \qquad D^*_{mn} = D^*\, \delta_{mn} \tag{5.22}$$

the relation between the concentration gradients in the exterior and the interior of the inclusion depends only on the shape of the inclusion and can be written in the form (Shchelchkova 1974, Salganik 1974, Landau, et al. 1988)

$$D^0 s_i = D^0 s_i^* + n_{ik}\left(D^* - D^0\right) s_k^* \tag{5.23}$$

In (5.23) n_{ik} is the depolarization tensor (being an analogue to the Eshelby tensor in solid mechanics). The components of the depolarization tensor can be, in a general case, determined only after quadratures of complicated integrals. Anticipating application to crack-like defect it suffices to consider inclusions in the form of oblate spheroids, i.e. when lengths of the three principal axes of the spheroidal inclusion are

$$a_1 = a_2 = a \qquad \text{and} \qquad a_3 = b = \beta a \tag{5.24}$$

In this case the principal values of the depolarization tensor (see Landau and Lifshitz 1988) can be derived in form of simple expressions

$$n^{(z)} = \frac{1+e^2}{e^3}(e - tan^{-1}e) \quad , \quad n^{(x)} = n^{(y)} = m = \frac{1}{2}(1 - n^{(z)}) \tag{5.25}$$

where

$$e = \left[\left(\frac{a}{b}\right)^2 - 1\right]^{1/2} \tag{5.26}$$

Therefore, the depolarization tensor can be written in form

$$n_{ik} = m\,\delta_{ik} + (1 - 3m)\,\delta_{i3}\,\delta_{k3} \tag{5.27}$$

The expression (5.23) generalized for all three axes is then

$$\left\{\left[1 - (1 - \eta)\,m\right]\delta_{ik} - (1 - \eta)(1 - 3m)\delta_{i3}\delta_{k3}\right\}s_k^{*'} = s_i' \tag{5.28}$$

or

$$(A_{ik}')^{-1}\,s_k^{*'} = s_i' \tag{5.29}$$

where the second rank tensor **A** is the inverse of the bracketed term on the left hand side of (5.28). The primes denote reference to the local (principal) coordinate system of the inclusion.

Thus,

$$s_k^{*'} = A_{ik}'\,s_i' \tag{5.30}$$

The expression (5.30) is written in terms of the local (inclusion) coordinate system and must, therefore, be transformed to the global (specimen) coordi-nate system. The general transformation rule for a second order tensor is

$$A_{mn} = A_{ik}'\,g_{mi}\,g_{nk} \tag{5.31}$$

where the coefficients of the rotation tensor g   written below in the matrix form are functions of the Euler angles φ and θ

$$
[g] = \begin{bmatrix} -sin\phi & -cos\theta\,cos\phi & sin\theta\,cos\phi \\ cos\phi & -cos\theta\,sin\phi & sin\theta\,sin\phi \\ 0 & sin\theta & cos\theta \end{bmatrix} \tag{5.32}
$$

From the expressions (5.31) and (5.32), in conjunction with (5.28), after some relatively simple but cumbersome operations it follows that the tensor **A** acquires a relatively simple form of

$$
A_{mn} = A\delta_{mn} + Bn_m n_n \tag{5.33}
$$

where the following identities were utilized

$$
n_m = g_{m3} \quad \text{and} \quad g_{mi}\,g_{ni} = \delta_{mn} \tag{5.34}
$$

The constants A and B in (5.33) are

$$
\pi A = \frac{\eta - 1}{4 + (\eta - 1)m} \qquad \pi B = \frac{\eta - 1}{4}\left[\frac{1}{\eta - 2(\eta - 1)m} - \frac{1}{1 + (\eta - 1)m}\right] \tag{5.35}
$$

In deriving (5.35) the inclusion volume was taken as

$$
V^I = \frac{4}{3}\pi a^2 b = \frac{4}{3}\pi a^3 \beta \tag{5.36}
$$

with $\beta = \frac{b}{a}$ being the aspect ratio of the lengths of the spheroid axes.

For a low to modest concentration of ellipsoidal inclusions (such that the interaction of their external fields has a negligible effect on the average current) the contributions of each inclusion can be merely superimposed. In this case from (5.20), (5.22) and (5.33) follows a reasonably simple expression for the effective diffusivity in form of

$$D_{ik} = D^0 \left[\delta_{ik} + \sum_{(r)}^{N} f_{(r)} \left(A_{(r)} \delta_{ik} + B_{(r)} n_i n_k \right) \right]$$

(5.37)

In the case of a large number of inclusions N the addition in (5.37) ceases to be a viable alternative. Instead, it is necessary to rewrite the expression (5.37) in form of an integral

$$D_{ik} = D^0 \left[\delta_{ik} + \int_Y \left(A \delta_{ik} + B n_i n_k \right) a^3 F \sin\theta \, d\phi \, d\theta \, da \, db \right]$$

(5.38)

In (5.38) the integration domain includes the solid angle $Y (0 < \theta < \pi/2 \ , \ 0 < \phi < 2\pi)$ and the entire range of the inclusion sizes. In contrast to (5.20) expression (5.38) implies that no correlation exists between the sizes, aspect ratios and orientations of inclusions. This seems to be a reasonable consequence of the inherent randomness of the hardened cement paste structure on the microscale. Thus, the normalizing condition (5.21) becomes

$$\int_Y F(\phi,\theta,a,b) \sin\theta \, d\phi \, d\theta \, da \, db = 4\pi \frac{N}{V}$$

(5.39)

In certain cases the sizes and orientations of the spheroids are not corre-lated allowing for a reasonably simple evaluation of the integrals in (5.38) and (5.39). It is important to notice that in the present case anisotropy stems only from the orientation of the inclusions since both the inclusions and the matrix are isotropic

The evaluation of the effective diffusivity (5.38) is even easier in the case of crack-like defects for which the parameter β tends to zero, while $\eta = D^*/D^0$ tends to infinity. Expanding the expressions (5.25) into Taylor series it follows that the parameter e tends to $1/\beta$. Thus, from (5.35)

$$A = -B = 1/\beta \quad \text{for} \quad 1 \gg \beta \gg 1/\eta$$

(5.40)

which significantly simplifies the computations.

In view of the fact that the inclusions occupy only a small part of the entire volume and in conjunction with the fact that the local strain is related to the average strain as the ratio of the total volume to the volumes of inclusions it seems reasonable to assume that the local stresses in the vicinity of the expanding inclusion are much larger that the average stresses. Consequently, it follows that the microcrack distribution is perfectly random (with respect to orientations and sizes). In the case of isotropic distribution of isotropic inclusions embedded in an isotropic matrix the diffusivity must be isotropic as well. Thus, the function F in (5.38-39) degenerates into a constant. In the considered case

$$F = 8\pi\beta\frac{\bar{N}\bar{a}^2}{V} \tag{5.41}$$

where the bar above the letter indicate average value. Thus, after relatively simple but laborious manipulations the effective diffusivity can be derived from (5.38) in a simple form of

$$D_{mn} = D\delta_{mn} \tag{5.42}$$

where

$$D = D^0\left(1 + \frac{32}{9}\omega\right) \tag{5.43}$$

with

$$\omega = \frac{N a^3}{V} \tag{5.44}$$

being the Budiansky-O'Connell (1976) micromechanical damage variable.

For the sake of completeness it should be noted that a different model for diffusivity was suggested by Whitaker (1967) who used the Taylor series expansion of the product $<v,c>$ about the vanishing convective velocity $<v> = 0$. The result turns out to be strikingly, if perhaps fortuitously, similar in form since according to the Whitaker's model

$$D_{jk} = D^0 (\delta_{jk} + B_{jk}) \tag{5.45}$$

where the second rank tensor **B** represents the effect of the tortuosity (irregularity of fluid paths and influence of the cracks, change in pore radii, etc.). An even more complex model using a fourth rank tensor

$$D_{ij} = a_{ijmn} \frac{v_m v_n}{|v|} \tag{5.46}$$

explicitly considers the microstructure of the continuum (through the tensor **a**) and convective velocity v (Nieman 1969).

The proposed model defined by expressions (5.38-39) for a general distribution of cracks, and (5.42-44) for an isotropic distribution of cracks, has a substantial advantage in comparison to other models which are basically phenomenological. Despite some uncertainties with regard to the determination of the number of cracks N and their size, shape and orientation distribution this model is firmly based on the micromechanics of the phenomena. Therefore, this model will readily allow future generalizations and extensions in quest of more rigorous and sophisticated analytical tools. For example, the model readily admits considerations of the influence of macrostresses and their sign (compressive versus tensile) on diffusivity (Salganik 1974), etc..

The unavoidable conclusion of this discussion is that a rigorous, deterministic derivation of the diffusivity is not a simple task. However, it is undeniable that the influence of the cracks on the diffusion patterns is substantial. For example, Bazant, et al. (1987) also suggest a formula according to which the diffusivity is proportional to the crack opening displacements and crack density which is in spirit identical to the expression (5.43). This formula was found to fit the experimental results rather well. Consequently, it seems plausible to conclude that the diffusivity is, indeed, proportional to the microcrack density, as suggested by (5.43). However, the determination of the constant of proportionality will at this point be made by fitting the experimental data.

It is finally important to note that the determination of the diffusivity of undamaged concrete is a problem in itself since the diffusivity of the thin transition zones (at the aggregate-cement matrix interface) strongly influences the flow patterns. In a virgin concrete these zones do not communicate. However, as the cracks evolve and start propagating through the cement paste they establish percolation paths which can disproportionally increase the macro-diffusivity.

Thus, the effect of microcracking may, indeed, be even more pronounced than expected. This is especially true in the vicinity of the percolation threshold.

6. STRESS-STRAIN RELATIONSHIP

Central to the investigations of the durability of concrete structures is the determination of the macro-stresses and macro-strains in the hardened cement paste associated with the expansion of the reaction products and the attendant microcrack nucleation and growth (damage evolution). On the micro-scale chemical reaction (4.2) takes place in small parts of the volume in the surrounding the pores with geometry conducive to the crystallization of ettringite. In general, the crystals will not form in subcapillary pores (in which the surface forces extend across the entire pore cross section, Hansen 1968). The expansion pressures will not build up in the pores open to the exposed surface, either. Consequently, the crystals capable of nucleating cracks will form only in a rather small part of the total volume.

The present task consists in determining the compliance of the hardened cement paste containing an ensemble of expanding crystals and an ensemble of microcracks. At this point it will be assumed that all expanding crystals are spherical in shape and that all cracks are penny-shaped. Consistent to the analyses in the preceding section, it will be again assumed that the defect concentration is low to moderate rendering their direct interaction inconsequential. It will also be assumed that the pore pressures have no appreciable effect on the stress-strain relationship (see, for example, Biot 1973, Rice and Cleary 1976, etc.).

6.1. Spherical inhomogeneities

Consider an isotropic spherical inhomogeneity (occupying domain Ω) with elastic properties defined by a symmetric fourth rank tensor C^*. The free expansion strain within the inhomogeneity, attributable to the difference between the volumes of reactants and the reaction product (ettringite) is denoted by $\varepsilon^r(x \in \Omega)$.

The free expansion strain within the inhomogeneity is, naturally, equal to one third of the volumetric expansion e^V (defined by the expression (4.8)). The enveloping matrix (hardened cement paste), occupying the domain $(V - \Omega)$, is also isotropic, elastic and homogeneous (in its virgin, undamaged, state) with material properties defined by the symmetric fourth rank tensor C^0. Consistent with the previously employed notation the superscripts (0) and (*) stand for the reference to the matrix and the inhomogeneity, respectively.

According to the Eshelby's theorem the strains within an ellipsoidal inhomogeneity are homogeneous if the far-field stresses and strains are homogeneous as well. Using this theorem and compensating for the disparity between the elastic moduli tensors C^* and C^0 of the inhomogeneity and the matrix by an equivalent uniform eigenstrain $\varepsilon^*(x \in \Omega)$ within the inclusion it is relatively straightforward to determine the basic relations between the stresses and strains in the entire domain V. This approach has been comprehensively dealt with in the seminal work by Mura (1982) rendering a recital of all details within this Report superfluous. However, in order to make this Report self-contained and self-sufficient the major points of the requisite analyses, specific to the problem at hand, will be duly highlighted in the text below.

Denote by

$$\varepsilon^{**} = \varepsilon^* + \varepsilon^r \tag{6.1}$$

For an isotropic, spheroidal inhomogeneous the eigenstrains ε^{**} are related to ε^r and far field deviatoric strain ε'^0 by (Mura 1982)

$$\dot{\varepsilon}_{ij}'^{**} = 15(1-v)\left[\dot{\varepsilon}_{ij}'^0 (\mu^* - \mu) - \dot{\varepsilon}_{ij}'^r \mu^*\right] \left[(5v - 7)\mu - (8 - 10v)\mu^*\right]^{-1} \tag{6.2}$$

where μ is the shear modulus. Also, the spherical parts of the strain tensors are related by

$$\varepsilon_{kk}^{**} = 3(1 - v)\left[(K^* - K)\varepsilon_{kk}^0 - K^*\varepsilon_{kk}^r\right] \left[(4v - 2)K - (1+v)K^*\right]^{-1} \tag{6.3}$$

where

$$K = \lambda + \frac{2\mu}{3} = \frac{E}{3(1-2v)} \tag{6.4}$$

is the bulk modulus of the matrix.
In (6.2)

$$\varepsilon_{ij}^{'0} = \varepsilon_{ij}^{0} - \frac{1}{3} \delta_{ij} \varepsilon_{kk}^{0} \tag{6.5}$$

are the deviatoric components of the far-field strains. The moduli μ and K without superscripts refer to the matrix.

The expression (6.3) can be further simplified if

$$\left(K^* - K\right)\varepsilon_{kk}^{0} < K^* \varepsilon_{kk}^{r} \tag{6.6}$$

The inequality (6.6) will be satisfied if:

- the bulk moduli of the ettringite and the hardened cement paste do not significantly differ from each other, and/or when

- the far-field strain is not the result of mechanical loads but arises from the accommodation of strains attributable to a dilute concentration of expanding inhomogeneous inclusions (beam or slab effect).

In absence of data regarding the elastic moduli of the ettringite it is not possible to estimate how much do they actually differ from those of the hardened cement paste. However, since the dilute concentration of inhomogeneous inclusions is actually the one examined within this Report the local strains must indeed be much larger in magnitude than their averages. Thus, from (6.3) and (6.6) in conjunction with (4.8) it further follows for a single ettringite inclusion that

$$\varepsilon_{kk}^{**} \approx \frac{-3(1-v)K^*}{(4v-2)K - (1+v)K^*} \frac{\varepsilon_{kk}^{r}}{f^I} = \frac{-3(1-v)K^*}{(4v-2)K - (1+v)K^*} \frac{\beta_1}{f^I} c_e \tag{6.7}$$

where the volume fraction f^I of inclusions is a positive number not larger than unity.

Assuming further, for simplicity, that the elastic moduli of the inhomogeneous inclusion (ettringite) and the enveloping matrix (hardened cement paste) are identical, it is not difficult to deduce that in the absence of the far-field stresses (from some other source), the strains inside a spherical inclusion are

$$\varepsilon_r = \varepsilon_\theta = \frac{1}{3} \frac{1+\nu}{1-\nu} \beta c_e \qquad , \qquad x \in \Omega \tag{6.8}$$

Outside the spherical inclusion of a radius a the strains are

$$\varepsilon_r = -\frac{2}{3} \frac{1+\nu}{1-\nu} \left(\frac{a}{r}\right)^3 \varepsilon^r \tag{6.9}$$

$$\varepsilon_\theta = \frac{1}{3} \frac{1+\nu}{1-\nu} \left(\frac{a}{r}\right)^3 \varepsilon^r \qquad , \qquad x \in (V - \Omega) \tag{6.10}$$

where in view of (4.8)

$$\varepsilon_{ij}^r = \varepsilon^r \delta_{ij} = \frac{1}{3} e^V \delta_{ij} \tag{6.11}$$

is the free expansion strain computed from the stoichiometric analyses in the Chapter 4 of this Report. It is notable that the inclusion expansion can impart large tensile hoop strains (6.10) capable of crack nucleation at the inclusion - matrix interface $(r = a)$

At this point it is tacitly assumed that the temperatures generated during the reaction are a second order effect in computations of the inclusion expansion. This point may have to be revised subsequently since the measurements indicate that a rather large thermal energy of 1450J per 1kg of the reaction product is liberated during a similar reaction taking place during hydration of the cement in the fresh cement paste (see Mchedlow - Petrosian 1988).

As the solute diffuses through the specimen the chemical reactions and the attendant crystallization of the ettringite will take place in a large number of locations surrounding the fluid conducting pores. The exact sizes, shapes and locations of the expanding inclusions containing ettringite crystals (which can exert substantial forces on the surrounding hardened cement paste) are generally not known. Consequently, it is not possible to consider every inclusion and superimpose the effects of all inclusions in the specimen to compute the average

stress and strain fields. Similarly as in the Chapter 5 of this Report this problem is typically resolved within the effective continua approximation framework discussed in great detail in Mura (1982) and Kunin (1983). As was mentioned before this approach has undeniable merits in the regimes preceding the critical phenomena but is, in its conventional form, of limited utility thereafter.

Consider, therefore, a volume V containing a dilute concentration of spherical inclusions having a total volume of

$$V^I = f^I V \tag{6.12}$$

The volume of inclusions is obviously proportional to the concentration of ettringite to the third power

Since the volume average of the stress perturbations (induced by inhomogeneous inclusions) about their average must by definition vanish the far-field stress must be equal to the average stress. It is then possible to show (Mura 1982) that the average strain attributable to the expanding inclusions is

$$\langle \varepsilon_{ij} \rangle = f^I \varepsilon_{ij}^{**} \tag{6.13}$$

The angular brackets in (6.13) are used to denote the average (expected) value of the bracketed variable. Knowing ε' from (4.8) and (6.11) it is then possible to compute from (6.7) ε^{**} and from (6.13) the average strain in the material point.

Combining (6.7) and (6.13) it further follows that the strain due to expanding inhomogeneous inclusions is directly related to the ettringite concentration c_e. The spherical part of the strain tensor (6.13) is then

$$\langle \varepsilon_{kk} \rangle = 3\beta c_e \tag{6.14}$$

where from (6.7) and (6.13)

$$\beta = \frac{-3(1 - v)K^*}{(4v - 2)K - (1 + v)K^*} \beta_1 \tag{6.15}$$

For the case of many inclusions the bulk modulus K in (6.7) is that of the effective continuum (matrix and the embedded inclusions). Unfortunately, neither

the self-consistent scheme (Budiansky 1965) nor the differential method (Hashin 1988) do not lead to an explicit expression for the effective bulk modulus. For the present purposes it is, therefore, more convenient to apply either the Voigt's (upper bound)

$$K_V = \left(1 - f^I\right) K^0 + f^I K^*$$
(6.16)

or Reuss' (lower bound)

$$\frac{1}{K_R} = \frac{1 - f^I}{K^0} + \frac{f^I}{K^*}$$
(6.17)

estimate. In the present case these two estimates should not be too far apart since $f^I \ll 1$. In (6.16) and (6.17) the indices V and R stand for Voigt and Reuss estimates.

The Voigt and Reuss expressions for the shear moduli are identical in form to ones for the bulk moduli, i.e. (see Mura 1982)

$$\mu_V = (1 - f^I)\mu^0 + f^I \mu^*$$
(6.18)

and

$$\frac{1}{\mu_R} = \frac{1 - f^I}{\mu^0} + \frac{f^I}{\mu^*}$$
(6.19)

The elastic modulus and Poisson's ratio can subsequently be computed from the expressions

$$\bar{E} = 2(1 + v)\mu$$

$$\bar{v} = \frac{3K - 2\mu}{2(3K + \mu)}$$
(6.20)

in either Voigt's or Reuss' approximation.

6.2 Cracks

The second type of defects consist of cracks of different sizes, shapes and orientations. For simplicity it will be assumed that the cracks are all planar and penny-shaped, but of different orientation. In this case a crack can be modeled as a oblate spheroid of vanishing thickness. The eigenstrain in such an inclusion is (Mura 1982, Krajcinovic and Sumarac 1987)

$$\lim_{a_3 \to 0} \left(a_3 \, \varepsilon_{3i}^{*} \right) = b_i' \, n_3' \qquad \text{(no summation)} \qquad (6.21)$$

In (6.21) a_3 is the vanishing thickness of the oblate spheroid (penny-shaped crack), $\mathbf{n}$ normal to the crack surface and $\mathbf{b}$ the displacement discontinuity across the crack plane. Primes indicate the local (crack) coordinate system selected in such a manner that the axis 3 is collinear with the normal to the crack surface.

Assuming that the crack during its growth remains in the same plane (i.e. that its growth is in our case self-similar) the displacement discontinuity can be written in form (Hoenig 1978)

$$b_i' = \left[1 - \left(x_j' / a_j' \right)^2 \right]^{1/2} B_{ik}' \, \sigma_{3k}' \, a_1 \qquad (6.22)$$

where a is the crack radius, $x_j' < a_j$, while $\mathbf{B}$ represents a matrix of influence coefficients which depend on the elastic parameters of the effective continuum (i.e. original matrix and the already existing cracks). The original matrix, naturally, includes the isotropic, but not necessarily homogeneous, distributi-on of the ettringite inclusions. Also σ is the external stress field which is in the spirit of the self-consistent method assumed to be equal to the macro-stresses σ^0.

Rewriting (6.21) in a symmetric form for the k-th crack

$$a_3 \, \varepsilon_{ij}^{*\,(k)} = \frac{1}{2} \left(n_i \bar{b}_j' + n_j \bar{b}_i' \right)^{(k)} \qquad (6.23)$$

averaging the displacement discontinuity over the crack surface

$$A\bar{b_i}' = \int_A b_i' \, dA \tag{6.24}$$

and introducing the coordinate transformation relating the local (crack) and global (specimen) coordinate systems

$$b_i' = g_{ij} b_j \qquad \text{and} \qquad \sigma_{ij}' = g_{im} g_{jn} \sigma_{mn} \tag{6.25}$$

(where the matrix $[g]$ is defined by (5.32)) the eigenstrain can be shown to be of the following simple form (Krajcinovic and Sumarac 1987, etc.)

$$\varepsilon_{ij}^{*\,(k)} = a_k^3 \, b_{ijmn} \, \sigma_{mn}^0 \tag{6.26}$$

The stress tensor imposed symmetries require

$$b_{ijmn} = \beta_{ijmn} + \beta_{ijnm} \tag{6.27}$$

where

$$\beta_{ijmn} = \frac{\pi}{3} B_{pq}' \left(g_{pi} g_{qn} n_m n_j + g_{pj} g_{qn} n_m n_i \right) \tag{6.28}$$

The transition to a large number of cracks is performed in the spirit of the effective continuum models in the manner discussed in the preceding chapter of this Report. The total strain averaged over the volume of the representative element V is then (Mura 1982)

$$\frac{1}{V}\int_V \left(\varepsilon^0 + \varepsilon \right) dV = \frac{1}{V} S^0 : \int_V \left(\sigma^0 + \sigma \right) dV + \frac{1}{V} \sum_k \int_{V_{(k)}} \varepsilon^* \, dV \tag{6.29}$$

where the stresses and strains without superscript indicate perturbations induced by the cracks. Since the average values of these perturbations vanish, and since

the far-field stresses and strains (denoted by the superscript '0') are at the same time the expected values from (6.29) and (6.26) it further follows that

$$\varepsilon^0 = \left[S^0 + \sum (a^3 / V) \mathbf{b} \right] : \sigma^0 = \mathbf{S} : \sigma^0 \tag{6.30}$$

where

$$\mathbf{S} = \mathbf{S}^0 + \sum (a^3 / V) \mathbf{b} = \mathbf{S}^0 + \left\langle \frac{Na^3}{V} \mathbf{b} \right\rangle \tag{6.31}$$

is the effective compliance. The angular brackets denote again the volume averages. Assuming that no correlation exists between the sizes and shapes of the cracks the effective compliance can be written in a simpler form

$$\mathbf{S} = \mathbf{S}^0 + \left\langle \frac{Na^3}{V} \right\rangle \left\langle \mathbf{b}(\theta) \right\rangle \tag{6.32}$$

According to (6.32) the compliance depends linearly on the Budiansky-O'Connell (1976) damage variable already defined by (5.44). The data related to the ellipticity and orientation of the crack population are stored in the fourth rank tensor **b**. As in the preceding chapter in the case of many cracks the sum is typically converted into an integral taken over the probability density functions defining the sizes, shapes and orientations of the cracks within the representative volume elements

$$\mathbf{S} = \mathbf{S}^0 + \int_Y \mathbf{b}\left(\theta, \frac{a}{b}\right) \frac{a^3}{V} B(Y) \, dY \tag{6.33}$$

where the normalizing condition is the same as in (5.21)

$$\int_Y B(Y) \, dY = N \tag{6.34}$$

These integrals can in conjunction with some simplifying assumptions be computed in the closed form (Krajcinovic and Fanella 1986, Sumarac and Krajcinovic 1987, etc.). Assuming an isotropic ensemble of penny-shaped cracks

embedded in an isotropic and homogeneous elastic matrix the effective elastic moduli can be derived in a closed, but not explicit, form (Budiansky and O'Connell 1976, Sumarac 1987). Neglecting the influence of the Poisson's ratio the elastic modulus in a material point of the effective continuum is

$$E = \overline{E}\left(1 - \frac{16}{9}\omega\right)$$

(6.35)

where ω is the damage variable defined by (5.44), while $\overline{E}$ is the elastic modulus of the material with inclusions but without cracks (6.20).

The final expression (6.35) for the elastic modulus is valid for sufficiently dilute concentrations of inclusions and microcracks (i.e. when their direct interaction is a second order effect).

6.3. Stress-Strain Relationship

Combining the influence of the expanding ettringite inclusions and already formed cracks the relation between the macro-stresses and macro-strains can be rewritten as

$$\varepsilon^0 = S : \sigma^0 + f^I \varepsilon^{**}$$

(6.36)

The elastic modulus of the undamaged part of the matrix must reflect the influence of the ettringite inclusions (in Voigt's approximation)

$$E^0 = \left(1 - f^I\right)E_{cp} + f^I E_e$$

(6.37)

where the subscripts cp and e refer to the cement paste and ettringite crystal. Then,

$$\sigma^0 = S^{-1} : \left(\varepsilon^0 - f^I \varepsilon^{**}\right)$$

(6.38)

For the considered isotropic (one-dimensional) case the expression (6.38) acquires a simple form

$$\sigma^0 = \bar{E}\left(1 - \frac{16}{9}\omega\right)\left(\varepsilon^0 - \beta c_e\right)$$

(6.39)

where the coefficient β is obtained combining the expressions $(4.10)_1$ and (6.15).

The further analyses follow the conventional routes. The macrostrains must satisfy the equations of compatibility and requisite boundary conditions. Additionally, the macrostresses must satisfy the equilibrium equations and boundary conditions on stresses as required by the considered problem.

6.4. Damage evolution law.

The final step in establishing the mechanical constitutive theory is to formulate a kinetic law relating the evolution of the damage variable ω as a function of the other thermodynamic variables. Assuming that the cracking will occur in the exterior of the expanding inclusion it seems reasonable to expect that the cracks will grow out in the direction of the radius of the expanding ettringite crystal (assuming it to be spherical in shape).

For a two-dimensional crack-hole system shown in Fig.1 an approximate formula for the stress intensity factor reads (Murakami 1987, p.264)

$$K_I = \frac{2p\,R}{\sqrt{\pi(R+a)}}F_0\left(\frac{a}{R}\right)$$

(6.40)

where R is the pore radius, a the crack length, p the pressure within the hole. In (6.40) $F_0\left(\frac{a}{R}\right)$ denotes a correction factor. For $(a/R) \geq 2$ it follows that $F_0 \approx 1$ and the stress intensity factor takes a simple form

$$K_I = \frac{2pR}{\sqrt{\pi(R+a)}}$$

(6.41)

For a constant radius R_0 from the equilibrium in the sense of Griffith

$$a = 2\frac{p^2 R_0^2}{\pi E_0 \gamma} - R_0$$

(6.42)

where γ is the fracture (surface) energy of the hardened cement paste. Assuming that the fracture energy is not modified (reduced) by the adsorption process (Rice 1978) the expression (6.42) suffices for the determination of the crack length a as a function of known quantities.
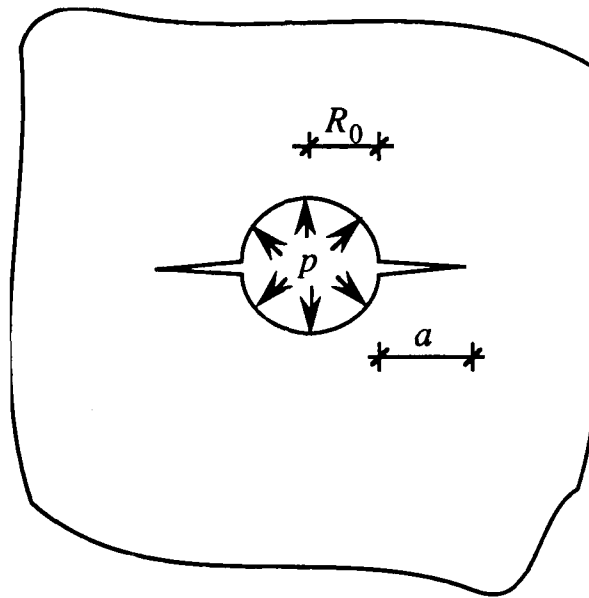

Fig. 1. Cracking due to expansion of an ettringite crystal.

A conventional analysis proves that

$$\frac{\partial G}{\partial a} > 0 \qquad \text{(unstable)} \quad \text{for} \qquad a < R_0 \qquad\qquad (6.43)_1$$

$$\frac{\partial G}{\partial a} < 0 \qquad \text{(stable)} \quad \text{for} \qquad a > R_0 \qquad\qquad (6.43)_2$$

In other words, the crack length vs pressure relation is discontinuous a shown in Fig. 2. A very small notch at the perimeter of the crystal will at one point become unstable and grow in a single spurt until it acquires the length $a = R_0$. After that the crack will increase its length with the added pressure in a monotonic and stable manner.
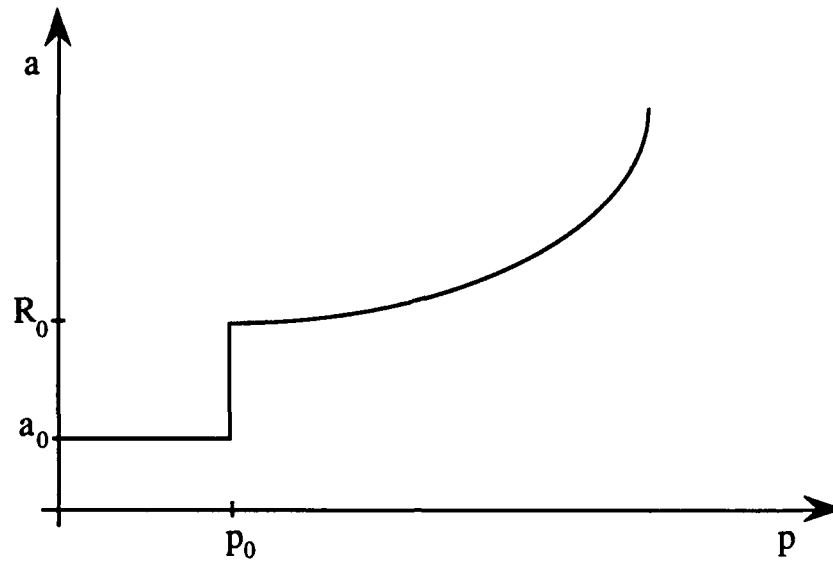
Fig. 2. Stability of crack growth

Since the pressure p within the pore is directly proportional to the volumetric expansion from (6.42) it follows that the crack length a is proportional to the square of the ettringite concentration c_e. Consequently, using (4.10) and (6.7) the damage parameter (5.44) is

$$\omega = g \, c_e^6 \tag{6.44}$$

where

$$g = \left(\frac{E}{\pi\gamma}\right)^3 \left[3R_0 \frac{\beta_1}{f^I} \frac{1-\nu}{1-2\nu} \frac{(K^*/K)}{(2-4\nu)+(1+\nu)(K^*/K)} \right]^6 \tag{6.45}$$

In (6.45) N denotes the number of cracks in the reference volume V, ν, E and K are the Poissons' ratio, the Young's modulus and the bulk modulus of the matrix, respectively; γ is the surface energy of the matrix. Superscript '*' refers to the ettringite.

It is quite apparent that a very precise and rigorous determination of all involved parameters entering above expressions is possible only in a statistical sense. Taking into the consideration that the inclusions are not spherical in shape

and that their size is not deterministic in nature it is, at this stage, not possible to be more explicit then to rewrite the expression (6.39) in the form

$$\sigma^0 = \bar{E}\left(1 - g_2 c_e^\S\right)\left(\varepsilon^0 - \beta c_e\right) = E\left(\varepsilon^0 - \beta c_e\right) \tag{6.46}$$

where g_2 and β are parameters to be determined from the expressions (6.35), (6.45), and (6.15). The expressions derived in this Report should provide guide and bounds for the determination of these parameters.

7. APPLICATION

The ultimate test of any analytical model is in its ability to replicate experimentally measured data and predict the response of a specimen or a structure. This task is in the present case hindered by: a less than precise documentation of the published test results, unfinished state of the model and the physical reality (i.e. essentially random nature of the phenomenon). The published test results generally lack precise data related to microstructural parameters (diffusivity, porosity, microcrack density, etc.) and are rather vague in defining what is actually considered to be the volumetric strain.

The best set of data related to the expansion of mortar specimens exposed to a combined external attack of $MgSO_4$ and Na_2SO_4 has been provided recently by Ouyang, et al. (1988) who performed their experiments in concert with the ASTM C1012 recommendations. Mortar specimens are used in such tests to accelerate the process of evaluating the potential expansion of the concrete elements in sulphate solutions (Price and Peterson 1968).

It is commonly observed that in the external sulphate attack the matrix cracking due to ettringite crystallization accelerates further penetration of new sulphate ions which, in turn, intensifies the pace at which the expansive ettringite is formed. The rate of the expansion is, thus, an increasing function of time, as demonstrated in Lea (1970, p.352, Fig.102) and Ouyang, et al. (1988, Fig.1). Conversely, in the case of internal sulphate attack the amount of sulphate ions that reside within the mortar decreases as the double decomposition reaction (4.1-2) proceeds. Consequently, the linear expansion versus time curves would exhibit

a decreasing slope, as reported by Ouyang et al.(1988). It should be mentioned here that the above observations refer to mortars and concretes made of ordinary portland cements. If, for example, silicate cements were used the expansion curves in the external sulphate attack would revealed a monotonically decreasing slope (Thorvaldson, et al. 1932, Lea 1970)

Consider the ASTM C490 test specimen used in the measurements of the length change, as shown in Fig.3a. Twenty four hours after casting the test bars are demolded, then cured in water while the companion mortar cubes are being tested for the compressive strength. If the required strength (20 MPa) has been attained the bars are placed in a mixed solution of 0.176 mol/L $MgSO_4$ and 0.176 mol/L Na_2SO_4.
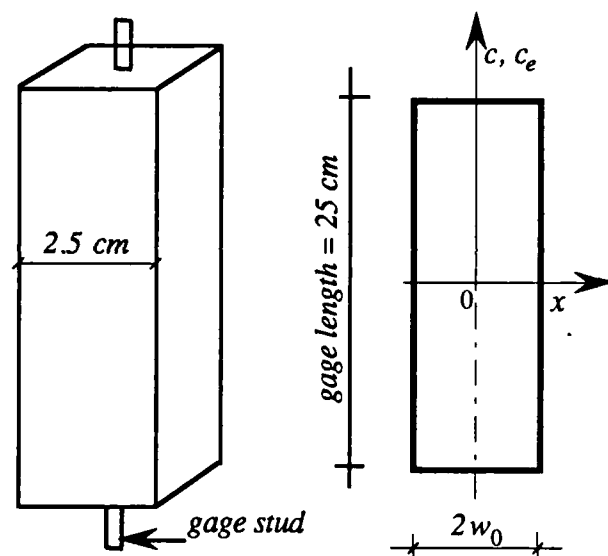
Fig.3 (a) ASTM recommended test specimen for measurements of the length change
(b) cross section of the specimen

The mix proportions of mortar and the content of tricalcium aluminate are usually given as the mass percentages with respect to cement. Therefore, it is necessary to convert the molar concentrations of sulphates to the mass percentages as well. Since the analysis is confined to the topochemical reaction

(4.2) the mass M of $V = 1\,m^3$ of mortar has been selected as the reference[1] . The mix proportions of the mortar used in Ouyang, et al. (1988) are

$$M_{cm} : M_{sa} : M_w = 1 : 4 : 0.6 \tag{7.1}$$

where the subscripts cm, sa, w denote cement, sand, and water, respectively.

Assuming the average values for the densities $\gamma_{cm} = 3150\,kg/m^3$, $\gamma_{sa} = 2650\,kg/m^3$ (Powers 1968) the amounts of the the constituent substances can be computed from the relation

$$\frac{M_{cm}}{\gamma_{cm}} + \frac{M_{sa}}{\gamma_{sa}} + \frac{M_w}{\gamma_w} = 1m^3 \tag{7.2}$$

neglecting the air content.

In the considered case the masses calculated from (7.2) are

$$M_{cm} = 412\,kg \quad M_{sa} = 1648\,kg \quad M_w = 247\,kg \quad ; \quad M = 2307\,kg \tag{7.3}$$

In order to determine the initial concentration of C$_3$A available for the reaction with the aggressive ions diffusing through the test specimen it is first necessary to estimate how much of the C$_3$A anhydride remains in the cement after the hydration. Assuming that the amount of gypsum added to portland cement clinker is 4% of M_{cm} (Biczok 1972 p.46) a true initial concentration of tricalcium aluminate is

$$f_a = \frac{M_{cm}}{M}\left(f_a' - 0.04\,\frac{m_a}{3\,m_g}\right) \tag{7.4}$$

where: $f_a' = (4.3\%, 7\%, 8.8\%, 12\%)$ is the C$_3$A content in the cement as given in Ouyang, et al. (1988); m_a and m_g are, as before, the molar masses of tricalcium aluminate and gypsum. The factor $(m_a / 3\,m_g)$ results from the stoichiometry of the reaction (4.2).

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[1] From now on the term **concentration** is to be understood as the mass percentage unless stated otherwise

The next step consists of computing the initial concentrations of sulphates with respect to the total mass M. The number of moles of both $MgSO_4\ 7H_2O$ and Na_2SO_4 in the saturated solution occupying the accessible pores is

$$n_{s1} = n_{s2} = n_s = \phi V \cdot 0.176 \ (mol / L) \tag{7.5}$$

where the subscripts s_1 and s_2 stand for $MgSO_4 \cdot 7\,H_2O$ and Na_2SO_4 respectively; $V = 1\,m^3$, while ϕ is, as before, the accessible porosity.

The total mass of sulphates in the considered volume becomes

$$M_s = M_{s1} + M_{s2} = n\,(m_{s1} + m_{s2}) \tag{7.6}$$

where m_{s1} and m_{s2} are the corresponding molar masses.

Taking in absence of exact data $\phi = 0.4$ as an average value for mortars and making use of (7.5) and (7.6) the initial concentration of sulphates is

$$c_0 = \frac{M_s}{M} = 0.012 \tag{7.7}$$

A tacit assumption on which the above analysis rests is that the action of magnesium sulphate and sodium sulphate on mortar is similar in the sense that both substances serve as sources for the aggressive ions SO_4^{-2}. In practice, the magnesium sulphate often turns to be more dangerous because it additionally attacks and decomposes hydrated calcium silicates (e.g. Lea 1970). On the other hand, it has been reported that a sodium sulphate solution is more corrosive than a magnesium sulphate solution if the calculated content of C_3A in the cement exceeds 9% (Biczok 1972 p.50). In the light of these information the assumption of an equal average influence of both substances on concrete corrosion seems justified.

Having computed the initial concentrations of reactants it is now possible to rewrite the rate equation for the ettringite formation (4.12)

$$\frac{dc_e}{dt} = k\left(\alpha c - \frac{3m_g}{m_e}c_e\right)\left(f_a - \frac{m_a}{m_e}c_e\right) \tag{7.8}$$

where c_e stands for the actual concentration of ettringite, αc is the initial concentration of the adsorbed gypsum, α the adsorption constant, and c the actual concentration of sulphates.

A rigorous analysis of the double decomposition chemical reaction (4.1-2) would require one kinetic equation for every substance entering the reaction. Expression (7.8), and in particular the assumption that the concentration of adsorbed gypsum and the sulphate are linearly proportional, is an attempt to simplify the analysis.

The experimental measurements of the rate constant k, for the observed chemical process, could not be found in the consulted literature. Thus, it becomes essential to devise means for a rational estimate of k based on available observations. For example, it seems reasonable to assume that the rate at which the considered reaction develops is similar to the rate at which the same reaction proceeds when the water is added to sand and cement during the mixing of mortar. For the latter case the rate equation is

$$\frac{dc_g}{dt} = k\left(c_g^0 - c_g\right)\left(f_a - \frac{m_a}{3m_g}c_g\right)$$

(7.9)

Knowing the initial concentrations of gypsum added to the clinker c_g^0 and the tricalcium aluminate f_a it is then possible to estimate the rate constant requiring that gypsum be consumed after a certain time t. Solving the equation (7.9) for k we get

$$kt = \left(f_a - \frac{m_a}{3m_g}c_g^0\right)^{-1} ln\left\{\frac{c_g^0[f_a - (m_a/3m_g)c_g]}{f_a(c_g^0 - c_g)}\right\}$$

(7.10)

Assuming, for illustration, that 50% of c_g^0 will be used up after $t = 24\,h$, the rate constant is computed from (7.10) to be $k = 2.4\cdot10^{-4}\,s^{-1}$. Naturally, since $k = k(\text{pressure}, T)$ the above estimate is based on the assumption that the temperature liberated by both reactions is identical and that k is not very sensitive to pressures (which are much higher during the formation of the ettringite in the hardened cement paste).

Finally it is advantageous to express (7.8) in a nondimensional form as follows

$$\frac{d\tilde{c}_e}{d\tilde{t}} = \tilde{k}\left(\alpha\tilde{c} - 0.412\,\tilde{c}_e\right)\left(\tilde{f}_a - 0.215\,\tilde{c}_e\right) \tag{7.11}$$

where:

$$\tilde{c}_e = \frac{c_e}{c_0} \qquad \tilde{c} = \frac{c}{c_0} \qquad \tilde{t} = \frac{t}{T} \qquad \tilde{k} = kTc_0 \qquad \tilde{f}_a = \frac{f_a}{c_0} \tag{7.12}$$

with c_0 given by (7.7), $T = 24$ h, and f_a defined by (7.4).

Consideration of the diffusion equation (5.15) in the actual three dimensional specimen requires costly and time consuming finite element computations. Even though these analyses may indeed become necessary at the later stages of the model development at this point they can hardly be justified. In order to assess the ability of the model to replicate the experimental trends it seems sufficient to consider the plane bisecting the specimen in Fig. 3b in halves and assume the diffusion to be one-dimensional (across the thickness only). In this case the diffusion equation (5.15) reduces to a much more manageable form of

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D^0\left(1 + g_1^{'}\omega\right)\frac{\partial c}{\partial x}\right] \tag{7.13}$$

where: ω is the damage variable (5.44).

The initial and boundary conditions are

$$c\,(x,0) = 0; \quad c\,(-w_0,t) = c\,(\,w_0,t) = c_0 \tag{7.14}$$

and additionally from symmetry

$$\frac{\partial c}{\partial x}(\,0,t\,) = 0 \tag{7.15}$$

which assures a smooth curvature of the concentration profile near the x-axis. In (7.14) w_0 is the half-width of the specimen cross section. Making use of the relation (6.44) the (7.13) becomes

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D^0\left(1 + g_1 c_e^6\right)\frac{\partial c}{\partial x}\right] \tag{7.16}$$

The ettringite concentration c_e is determined from the rate equation (7.8). The governing equations (7.8) and (7.16) are highly nonlinear and coupled rendering the analytical or even approximate solutions not possible at this time. From the numerical standpoint the analysis of the problem is further complicated by the fact that the system of rate equations (7.8) is quite stiff, to the point that even the Gear's method (commonly used in this class of problems) is not effective. At the present stage it seemed reasonable to use a somewhat less rigorous (partially uncoupled) approach. Assume at the very first time step that the diffusivity D is not affected by the microcracking $\left(\omega = 0 \implies D = D^0\right)$. Thus, the solution of the diffusion equation (7.16) can be expressed in the form of an infinite series (Carslaw and Jaeger, 1959)

$$\tilde{c}(\tilde{x},\tilde{t}) = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\left(\pi\tilde{x}\frac{2n+1}{2}\right)\exp\left[\frac{\tilde{D}\pi^2}{4}(2n+1)^2\tilde{t}\right] \tag{7.17}$$

where, consistent with (7.12), the following normalization was introduced

$$\tilde{c} = \frac{c}{c_0} \qquad \tilde{x} = \frac{x}{w_0} \qquad \tilde{t} = \frac{t}{T} \qquad \tilde{D} = \tilde{D}^0 = \frac{D^0 T}{w_0^2} \tag{7.18}$$

Computing the sulphate concentration $\tilde{c}$ from (7.17) it becomes now possible to solve the rate equation (7.11) for the ettringite concentration $\tilde{c}_e$. In the next time step this value is inserted into the expression for diffusivity $\tilde{D} = \tilde{D}^0\left(1 + g_1\tilde{c}_e^6 c_0^6\right)$, a new value of $\tilde{c}$ is found from (7.17), and the process repeated. If the time step is kept small this procedure is found to lead to a reasonable solution. The numerical code using the IMSL (1987) routines for the solution of a system of 21 coupled nonlinear ordinary differential equations (7.11) at the discretization points is

listed in the Appendix B. The CPU time consumed at one run of the program on IBM-3090/XA was about 3 minutes.

The existing experimental data are limited to measurements of the axial (or volumetric) strains averaged over the entire length of the specimen. Thus, the estimate of the accuracy of the analytical model are restricted to the comparisons of the computed and measured average strains.

In the absence of the externally applied tractions the average stresses in the cross section must vanish

$$\int_0^{w_0} \sigma(x, t)\,dx = 0 \tag{7.19}$$

Introducing further the classical Euler-Bernoulli's hypothesis of plane cross sections the overall strain can be computed from (6.46) in conjuction with (7.19)

$$\varepsilon = \beta c_0 \frac{\int_0^1 \tilde{c}_e(x,t)\,\overline{E}\left[1 - g_2(c_0\tilde{c}_e)^6\right]\,d\tilde{x}}{\int_0^1 \overline{E}\left[1 - g_2(c_0\tilde{c}_e)^6\right]\,d\tilde{x}} \tag{7.20}$$

where the normalized variables (7.12) and (7.18) have been used.

With the gradual increase in the microcrack density the elastic modulus (6.35) or (6.46) decreases. At one point the elastic modulus might vanish, i.e. the material becomes so heavily damaged that it looses its load carrying capacity. Consistent with the assumption that the local stresses around expanding inclusions are dominant (i.e. much larger than the stresses associated with the beam like behavior) the zone in which the load-carrying capacity is lost is contiguous with the external surface (Fig.4).

This type of behavior is often modeled introducing a fracture (or percolation) front, Fig.4 (cf. Kachanov 1986), separating the heavily damaged zone from the material which can still carry the loads. In fact such a behavior (spalling) is commonly observed in the structural elements exposed to aggressive waters (e.g. Biczok, 1972). The formulation of a proper criterion of the percolation front propagation is a complicated task considered to be beyond the

scope of this study. For the present purposes the position of the front will be identified with the plane in which the elastic modulus reaches the zero value. From (6.46) the position of the fracture front is

$$E = \overline{E}\left[1 - g_1 (c_\mathscr{E}^{cr})^6 \right] = 0 \tag{7.21}$$

where $c_\mathscr{E}^{cr}$ is the corresponding critical concentration of ettringite.
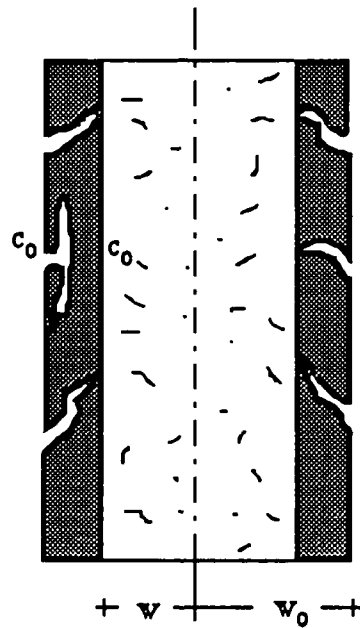
Fig. 4. Moving fracture (percolation) front.

Naturally it is well known that the criterion $E = 0$, or $\omega_{cr} = 9/16$, is but a sign that the accuracy of the self-consistent model deteriorates for $\omega \approx 0.5$ (see Hashin 1983). More sophisticated analyses (Kunin 1982, Christensen and Lo 1979, Hashin 1988) indicate that E does not vanish at $\omega = 9/16$ as indicated by the Budiansky-O'Connell (1976) analyses. However, the statistical studies of Hansen, et al.(1989) demonstrate that the failure does occur at $\omega \approx 0.5$ (at least for the two-dimensional lattice they considered). In other words, their results confirm that the crack interaction, and thus, stress redistribution in the pre-

critical domain are not crucial for the determination of the critical point. Whether this is actually true for a three-dimensional case cannot be assessed without a serious study of the corresponding percolation process. At this point, in view of other uncertainties and the limited objective of this Report it seems reasonable to adopt the simplest alternative and argue that the criterion (7.21) approximates the reality with a satisfactory accuracy. The post-critical behavior will be reduced to claiming that the stress in the volume swept by the front $|x| > w$ vanishes. In this manner the thickness of the narrow zone in which the concrete 'softens' before the stress actually vanishes is shrunk to zero.

In view of the condition (7.21) the formula (7.20) ceased to be valid when the percolation fronts are generated. At this point (7.20) should be replaced by an approximate expression as follows

$$\langle \varepsilon \rangle = \left(1 - \frac{w}{w_0}\right) \beta c_\varepsilon^{cr} + \frac{w}{w_0} \beta \frac{\displaystyle\int_0^w E(x,t) c_e(x,t) \, dx}{\displaystyle\int_0^{w_0} E(x,t) \, dx} \tag{7.22}$$

where $\langle \rangle$ stands for the average value. In (7.22) β is the expansion coefficient, while w and w_0 are specified in Fig.4.

Results of the performed computations are summarized in Figs 5 to 16. The following numerical values were assumed for the material parameters involved in the model: $D^0 = 10^{-8}$ cm^2/s (cf. Biczok 1972 p.141), $c_0 = 0.012$ (see 7.7), $k = 2.9 \cdot 10^{-5} s^{-1}$ (7.10), $\alpha = 0.8$, $\beta = 0.1$ (4.10$_1$ and 6.15), $f_a' = (4.3\%, 8.8\%, 12\%)$, $v = 0.2$, $K^*/K = 0.75$. The two fitting constants were assumed to be $g_1 = 0.5 \cdot 10^{12}$, $g_2 = 0.7 \cdot 10^{11}$.

The concentration of sulphates across the thickness of the specimen is plotted in Figs 5 and 6. For small volume fractions of C$_3$A (or short times) the sulphate concentration c is equal to c_0 only at the external surface of the specimen $(x/w_0 = 1)$. However, if the mortar spalls off near the surface the heavily damaged volume of the mortar immediately saturates as shown in Fig.6.

Similar situation, Figs 7 and 8, occurs with the concentration of ettringite obtained solving the equations of the kinetics of the chemical reaction (7.11). The main difference between two figures is in the chemical composition of the mortar

(i.e. mass of C_3A). The horizontal part of the ettringite concentration curve in Fig. 8 corresponds to the fractured zone in the specimen.

The change of diffusivity, depicted in Fig. 9, also shows the expected patterns. The two-fold increase of the diffusivity at the external surface (for the 4.3% C_3A content) is of the same order of magnitude as measured for a reinforced concrete beam by Bazant, et al.(1987). For this case of a 'sulphate resistant' composition the change of diffusivity is restricted to the vicinity of the external surface.

The reduction of the elastic modulus, shown in Figs 10 and 11, develops along the expected lines. The drop of ~20% for the mortar with 12% C_3A is in a good agreement with the experimental data from Ouyang, et al. (1988, Fig. 3). Naturally, consistent with the adopted model the elastic modulus reduces to zero in the part of the volume swept by the percolation front (Fig. 11). In the case of the sulphate resistant mortar, Fig. 10, the damage, i.e. drop in elastic modulus is again confined to the vicinity of the external surfaces.

The stress distribution across the specimen thickness is plotted in Figs 12 and 13. For the specimen with a safe mass fraction of C_3A (Fig. 12) large compressive stresses occur near the external surface while the middle part of the specimen is subjected to smaller tensile stresses. As soon as fracture (spalling) occurs the stresses drop to zero and the compressed zone shifts inward (Fig. 13). The computed values for macro-stresses indicate that the compressive macro-stresses are still below the levels at which they will influence the local stresses around the expanding inclusions. However, the tensile stresses in the middle portion of the specimen might indeed facilitate cracking and accelerate the failure. This aspect of the problem will be considered in the following stages of the program.

The propagation of the fracture (percolation) front for the case of a test bar with 12% of C_3A is plotted vs time in Fig. 14. In absence of experimental data this curve, while intuitively acceptable, cannot be confirmed in a quantitative sense. It is notable that the proposed model will, indeed, allow for the determination of the safe duration of the sulphate attack. In the considered case the exposures less than 60 days will not cause any spalling. Therefore, once thoroughly tested, this model may indeed prove to be a powerful design tool. Naturally, the model itself must be improved by introduction of a more realistic criterion for the onset of critical phenomena (percolation or spalling).

Fig. 15 represents the actual objective of this program, i.e. it tests the ability of the model in relating the macro-structural, phenomenological observation (macro-strain or expansion) and the chemical composition of the mortar. The curve for the lowest concentration of tricalcium aluminate (4.3%) is duplicated with a remarkable accuracy. For the mortars with a larger content of C_3A the trends are qualitatively duplicated but the fit, as expected, is somewhat less impressive. This is, naturally, the result of the fact that the spalling which occurs in these cases was not adequately modeled by the present theory. A less than rigorous selection of the mortar failure criterion ($E = 0$, i.e. $\omega = 9/16$) (7.21) and the attendant uncertainties with regard to the post-critical (softening) response of the mortar resulted in a quantitative discrepancies with respect to the measured data. This error is further compounded by the fact that a fluid path through a system of connected cracks (percolation threshold) will, in general, occur well ahead of the onset of fragmentation (Jaeger, private communication 1990). Thus, the transport of sulphates will occur in a mode combining diffusion (through the very thin pores) and percolation. As a result the expansion will be accelerated establishing a closer fit between the experimental and analytical data.

In conclusion, the data plotted in Fig. 15 demonstrate a remarkable ability of an as yet incomplete model in replicating the trends in a qualitative way, and provide a promise that a better than expected quantitative fit can be obtained once the model is completed.

In a chemical sense the reactions (4.1-2) in a mortar poor in tricalcium aluminate consume all of it without being able to generate enough expansion to endanger the integrity of the mortar. Once the C_3A is totally consumed the ettringite crystals will cease to expand and multiply and the mortar will remain immune to further exposure to sulphates (its strength will be somewhat reduced by the ettringite inclusions, see expressions (6.14) and (6.15)).

The graphs in Fig. 16 depict the increase in the ettringite concentration with time for mortars with three different C_3A contents. It can be seen that the response of mortars rich with C_3A was dominated by the supply of gypsum (first parenthesis in 7.11). Thus, in the case of continued supply of gypsum the expansion can be continued until the specimen fractures. In contrast the response of mortar with 4.3% of C_3A is limited by the available tricalcium aluminate (second parenthesis in 7.11). At one point, somewhat in excess of the considered duration of 60 months, the curve approaches a horizontal asymptote and the

specimen becomes impervious to further sulphate attack (see Mather 1968, Fig. 3).

The present computations were, for the discussed reasons, discontinued beyond $\varepsilon > 0.15\%$ since the lack of information regarding the behavior of mortar in the post peak region (which occupies the ever increasing part of the specimen volume) makes these computations incorrect. At the current state of development it was considered sufficient to demonstrate the trends of the response. Only the analyses in the case when the softening material occupies only a small part of volume can be considered rigorous. For the case when the softening material occupies a large part of the volume the present model offers only an approximate solution.

It should be emphasized again that the model in its present form contains two fitting parameters g_2 and g_1. In fact they could be determined from (6.44) if the involved micromechanical constants are known.

The value $\beta = 0.1$ for the coefficient of linear expansion used in the computations was obtained assuming (in absence of the experimental data) the ratio of the bulk moduli of the ettringite and mortar to be equal to 0.75. This corresponds to the ratio of the densities of two materials. It was also accounted for the fact that in the analyzed case the solution contains both magnesium and sodium sulphates in equimolar concentrations. The value for the rate constant k used in the computations was lower than the simplified estimate discussed on the page 48. To this end one has to bear in mind that the time needed for the first of the double-decomposition reaction (4.1-2) to complete has been neglected, while the actual form of the rate law for the second reaction was uncertain as well. However, the general structure of the model allows for the incorporation of any modification once convincing and specific experimental data become available.

8. SUMMARY AND CONCLUSIONS

Despite the fact that the theory is at this point not complete it, nevertheless, strongly indicates the inherent power of microstructural modeling. The major advantage of this type of modeling is in its ability to relate the chemical composition and microstructure (porosity, diffusivity, etc.) of the cementitious

composite to its performance under all conditions. This becomes abundantly clear in the case of the investigations described and summarized in this Report.

As shown in Fig.15 the model clearly distinguishes between the case of small concentration of tricalcium aluminate (which is sulphate resistant if less than 5.5%, Ouyang, et al. 1988) and the mortars rich in C_3A which disintegrate when subjected to water-borne sulphate for a prolonged time period. Naturally, similar analyses can be readily performed for an entire class of related problems such as processes driven by pressure gradients (flow through the porous media), alcali-aggregate reactions, cation-exchange reactions, hydrolysis of the cement paste, formation of insoluble and nonexpansive calcium salts, carbonic acid attack, frost action, etc.. The apparent ease with which the model succeeds in replicating the results of a complex physico-chemical process gives rise to considerable confidence in its utility and versality, and presents a strong impetus for its future development.

As it was duly noted in numerous places in this Report the model is by no means completed. A serious effort must be made to clarify a number of contentious arguments and remove some of the uncertainties. For example:

- The computations leading to results plotted in Fig.15 are, rigorously speaking, correct only for the curve with the lowest concentration of tricalcium aluminate. Even though some justification for the selection of the fragmentation (fracture) criterion ($\omega = 9/16$) is available a much more detailed and rigorous study of the critical phenomena and response of the mortar in the post-critical (post-peak or softening) regime must be undertaken in order to gain full confidence in the model.

- The computation of diffusivity without considering the formation of a direct path through a system of connected microcracks (which can happen at rather low microcrack densities and much before fragmentation) seriously underestimates the rate at which the process develops at the later stages of the deformation. This is quite obvious from the Fig.15 for the two mortars with higher concentration of tricalcium aluminate. Even though the trends of experimental data are well replicated the model underestimates the expansion by neglecting the percolation.

In conclusion, the proposed model formulated in the course of this AFOSR sponsored research program, shows undeniable promise and ability to deal with a complex and hitherto not well understood process. The elements of the proposed model are firmly based on the chemistry and physics of the process, as well as

the properties of the cementitious composite and its micro-structure. Once fully developed and tested, this model should contribute to the formulation of a potent tool for the optimization of the chemical composition of concrete in view of its purpose and the ambient to which the structure will be exposed. However, in order to reach this stage additional basic analytical and experimental effort cannot be avoided.
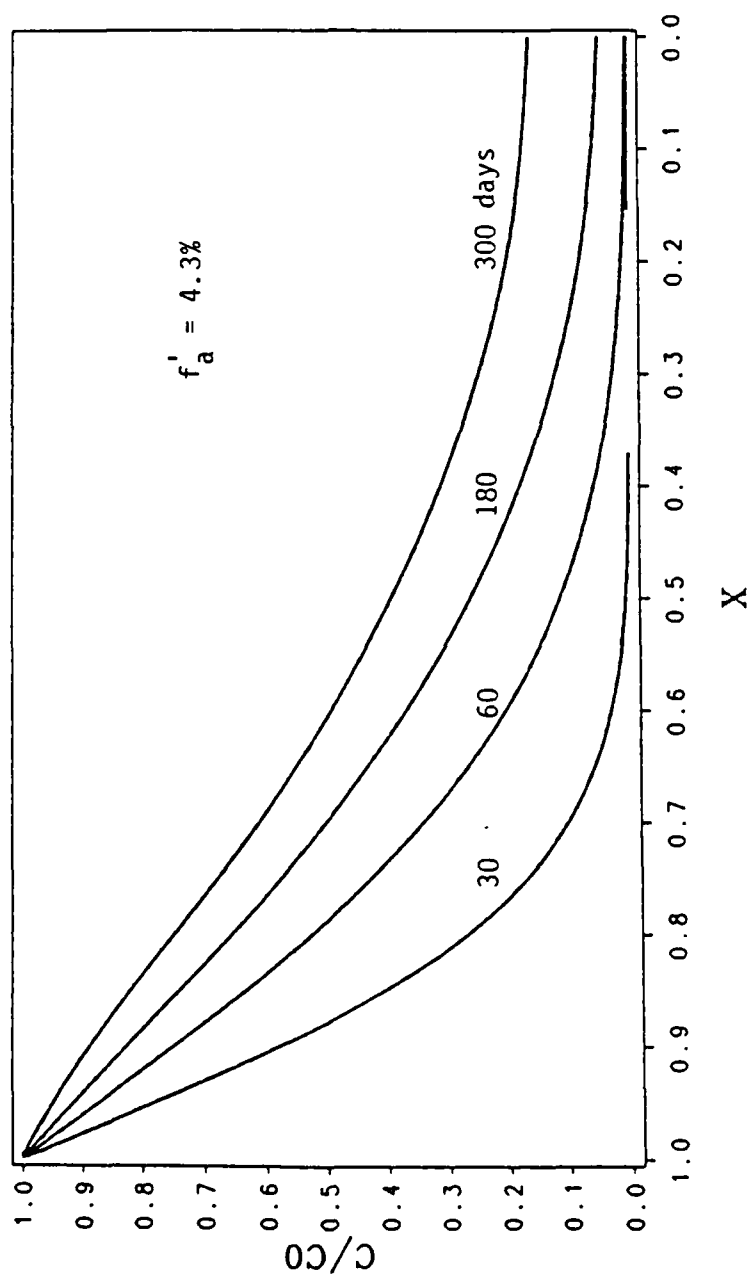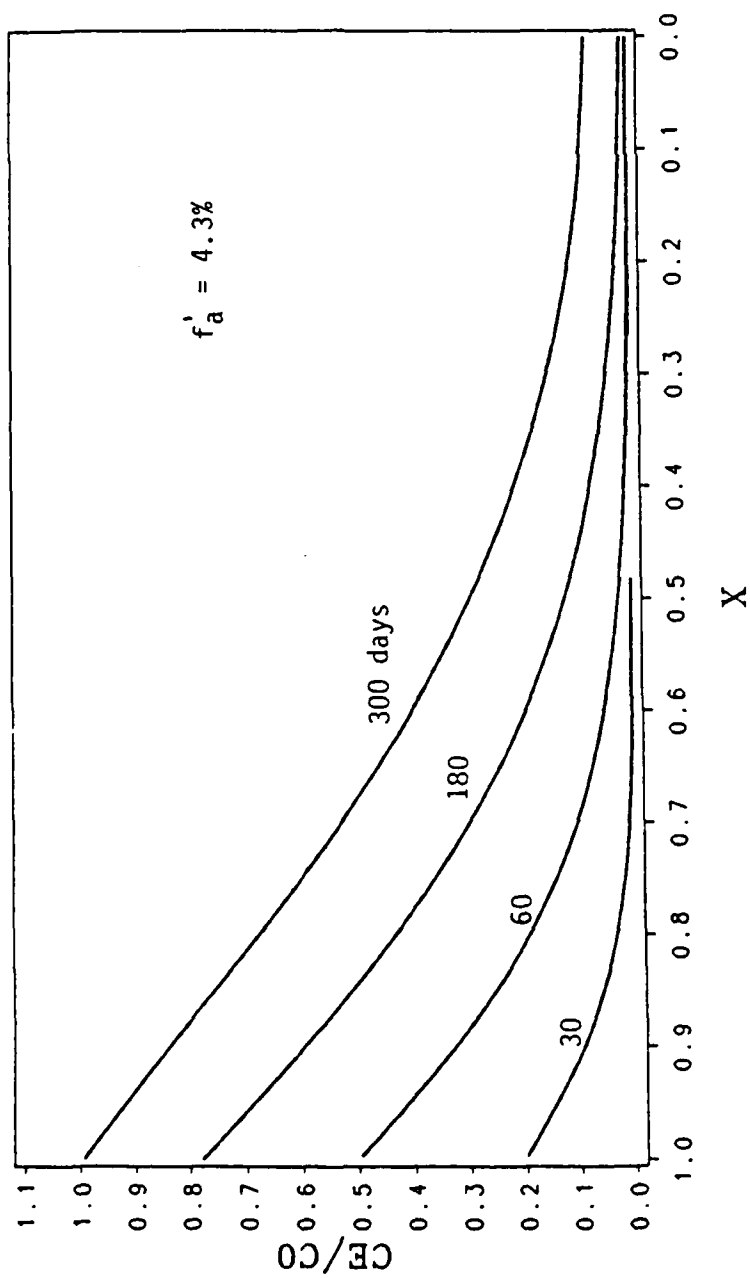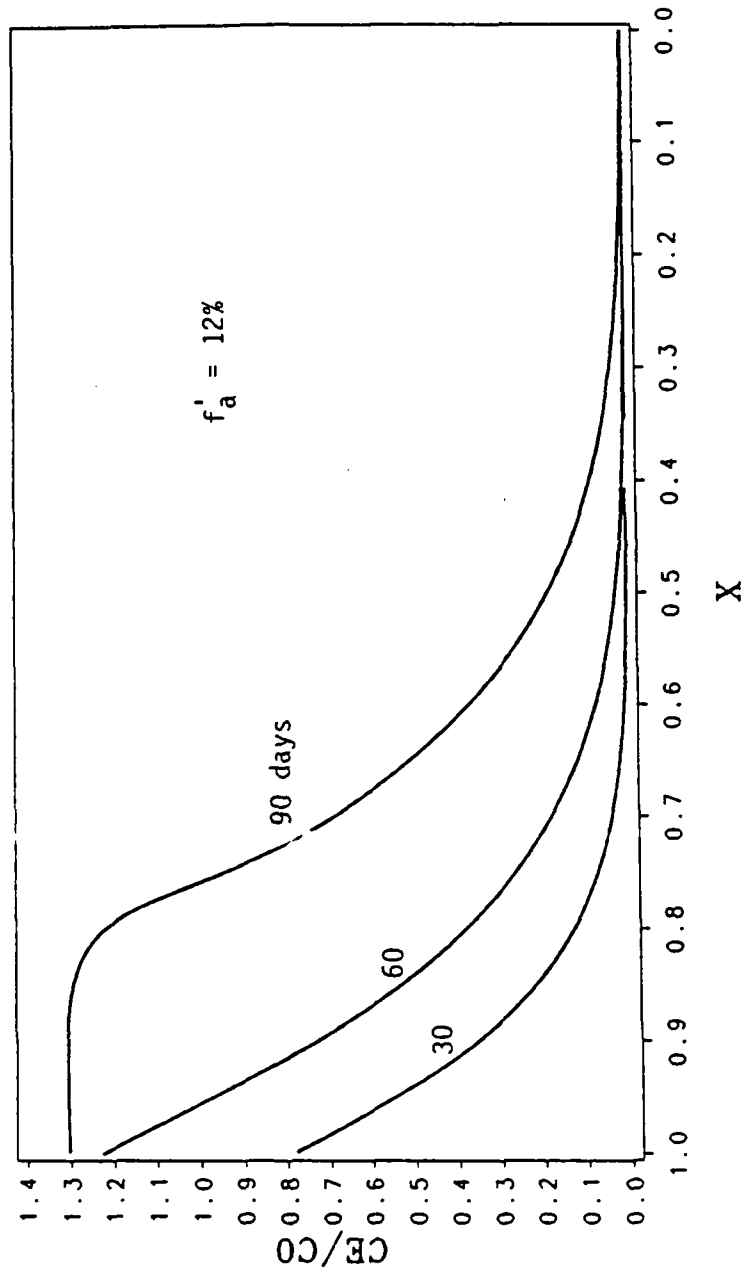
CONCENTRATION OF SULPHATES
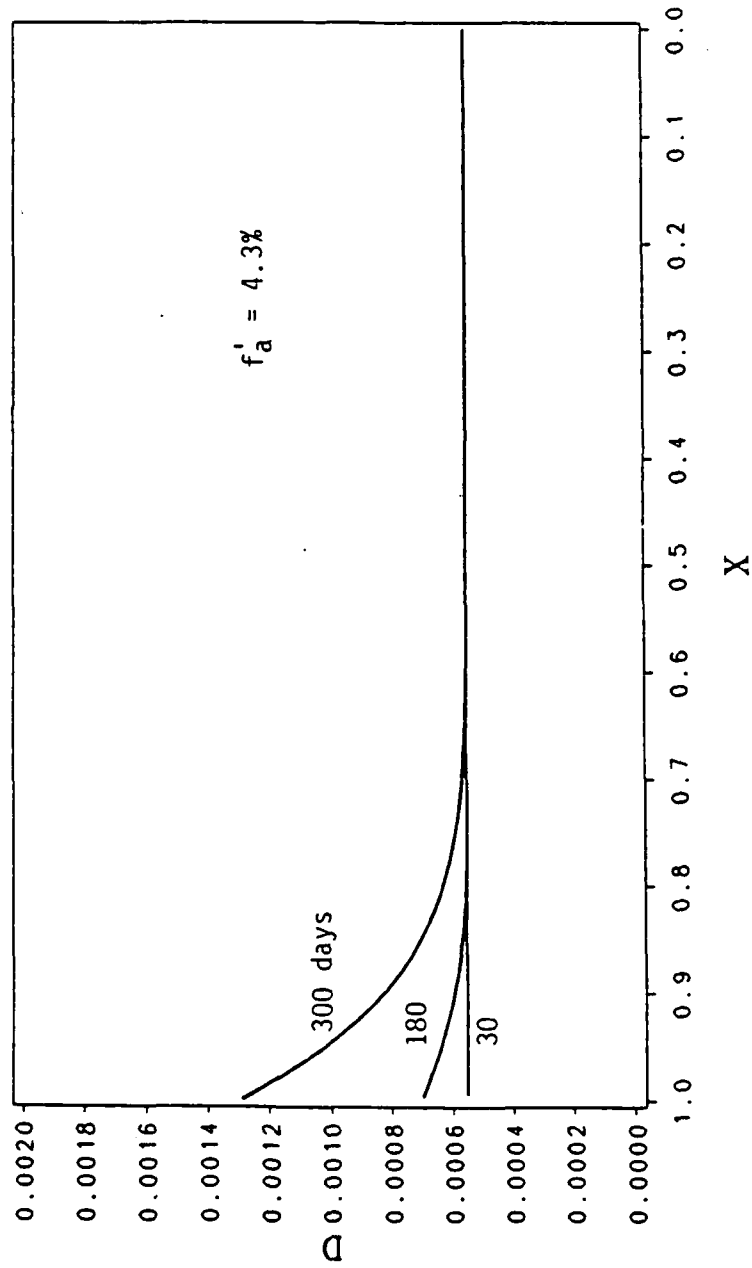
FIG. 5
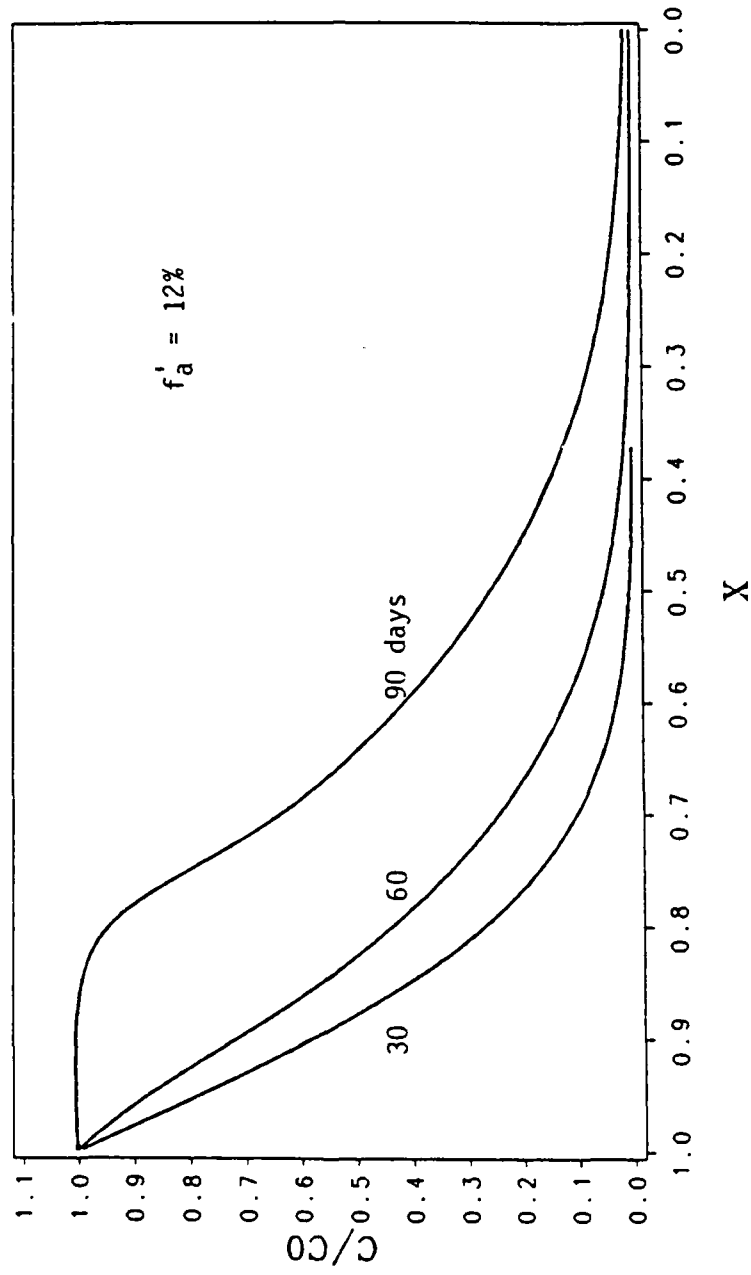
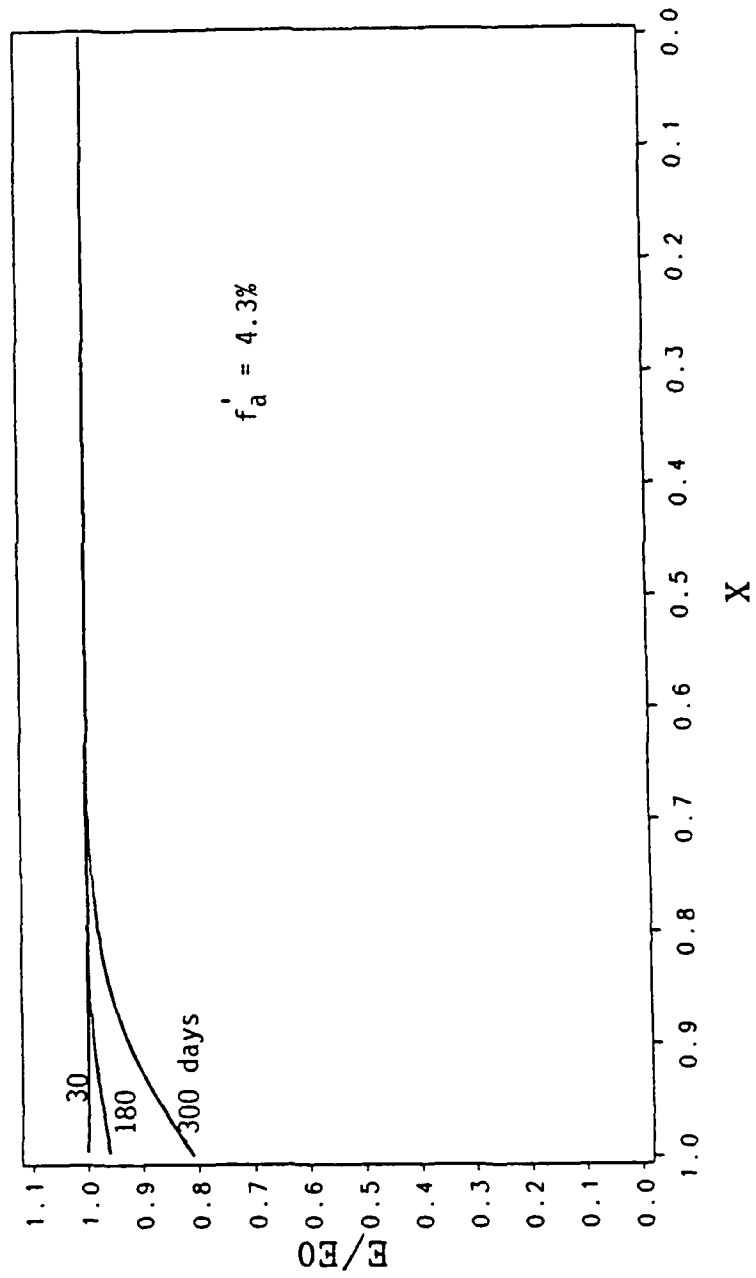CONCENTRATION OF SULPHATES

FIG. 6

CONCENTRATION OF ETTRINGITE

FIG. 7

CONCENTRATION OF ETTRINGITE

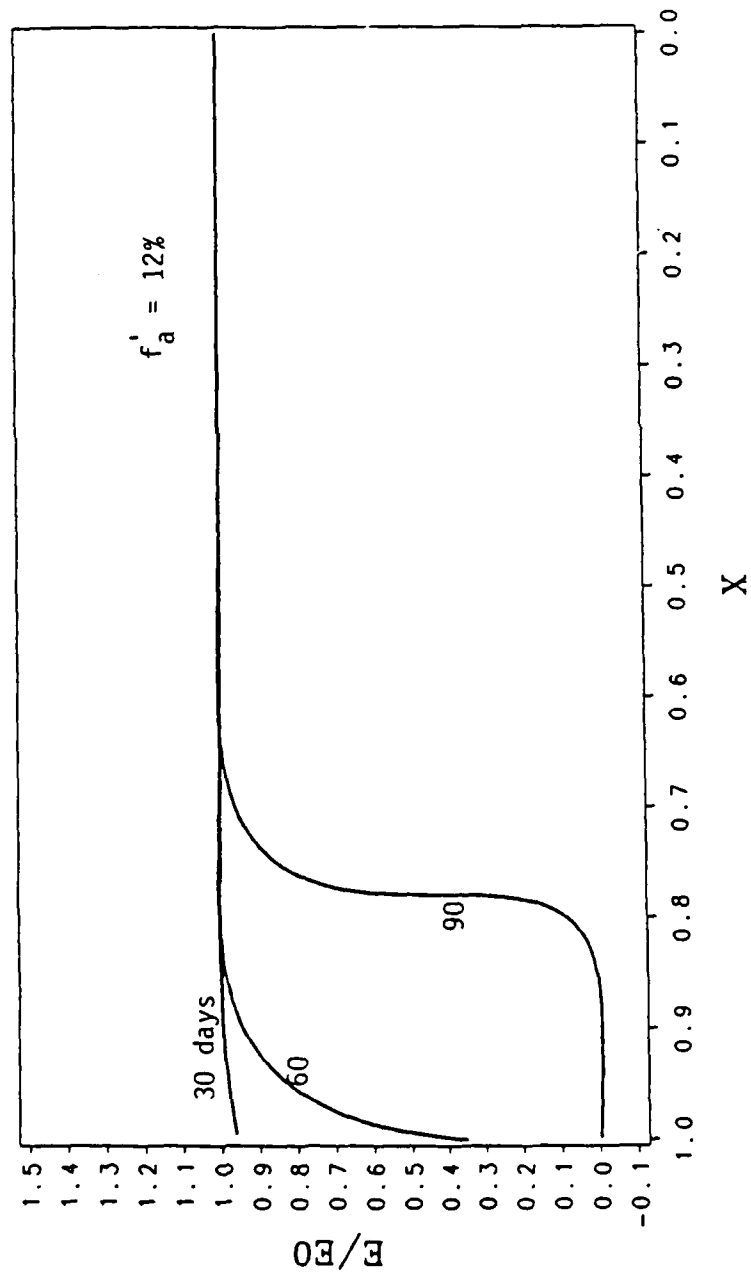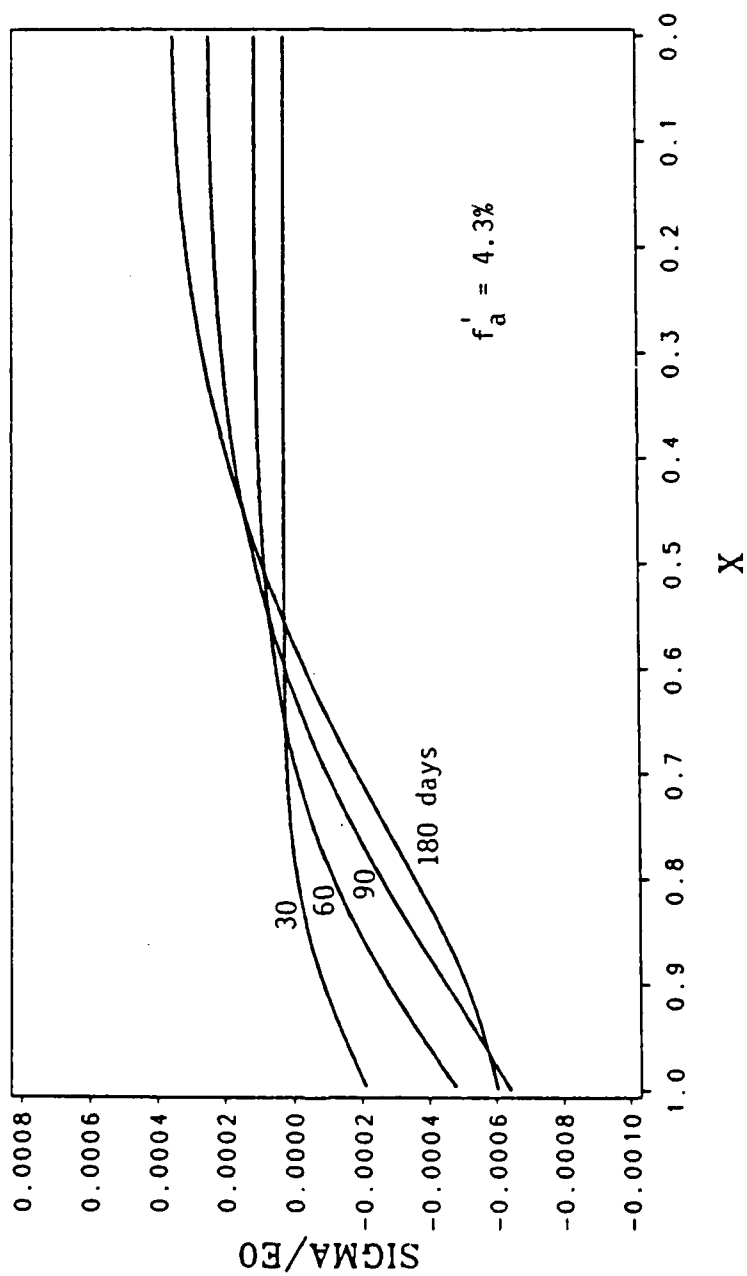FIG. 8

DIFFUSIVITY VARIATION

FIG.9

REDUCTION OF ELASTIC MODULUS

FIG.10

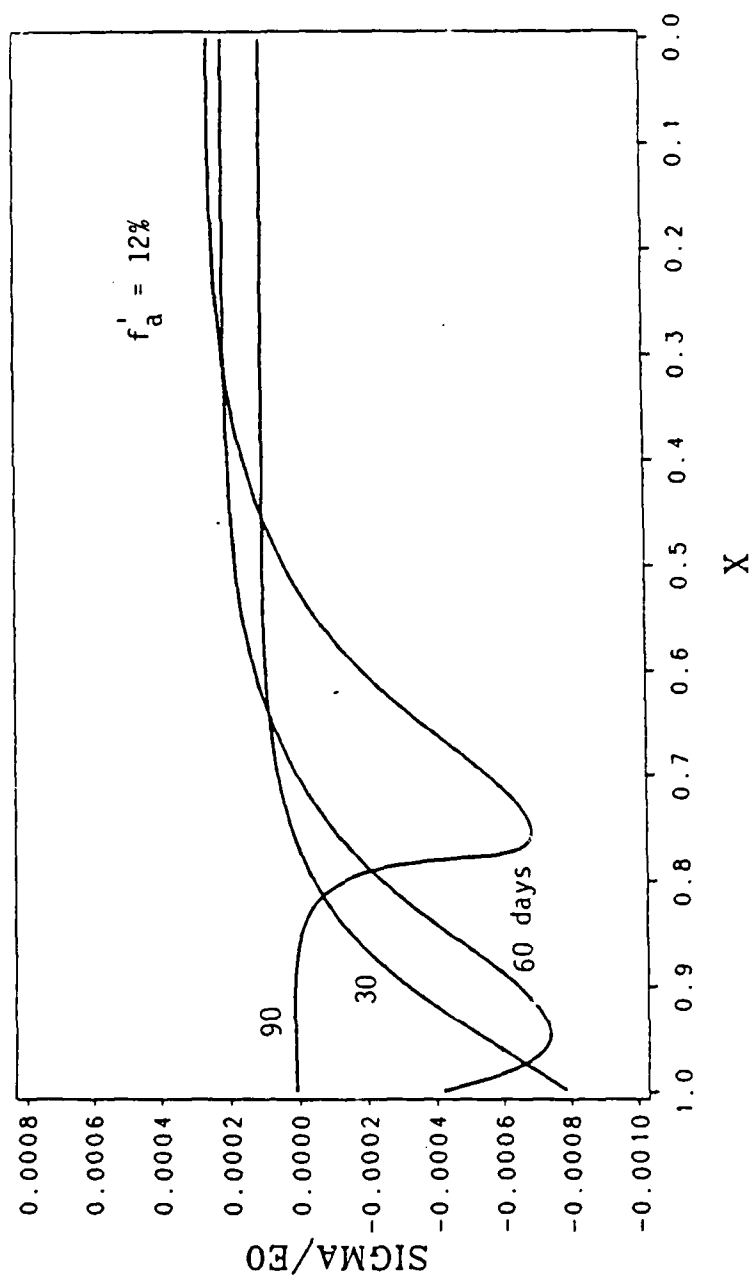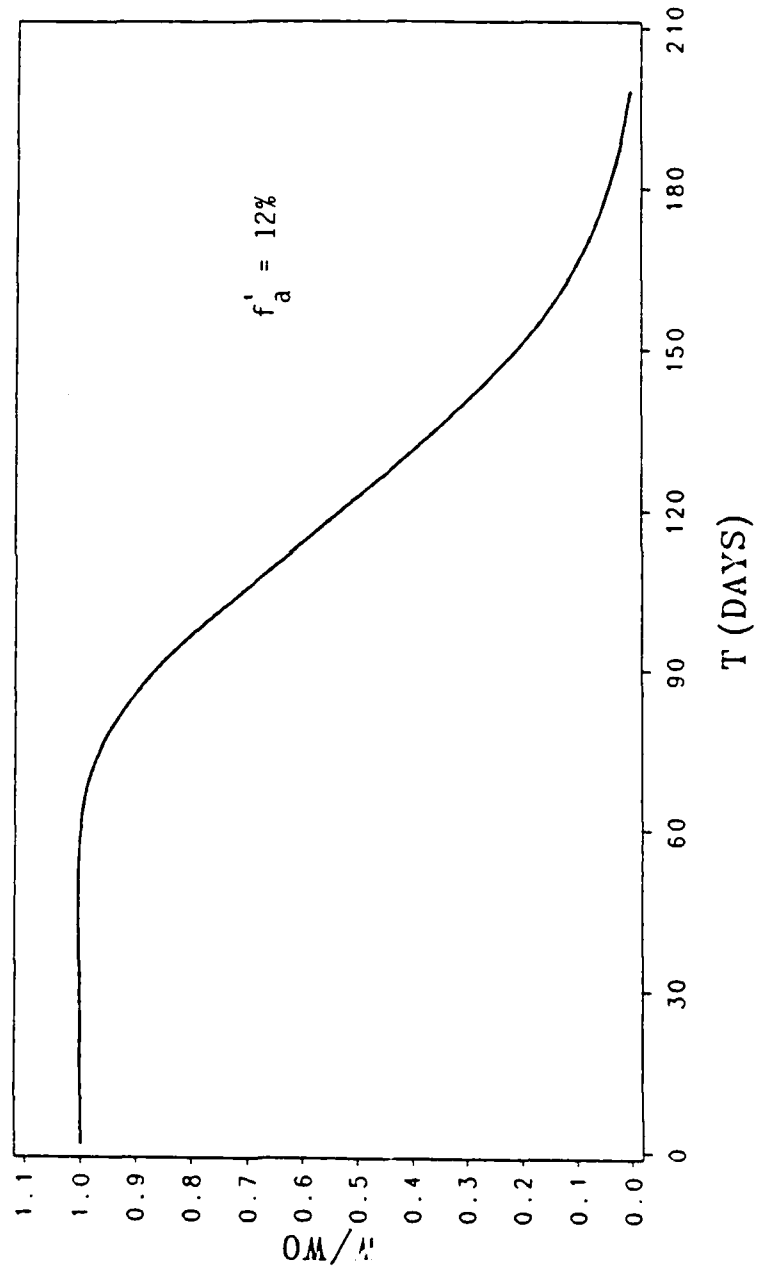REDUCTION OF YOUNG MODULUS

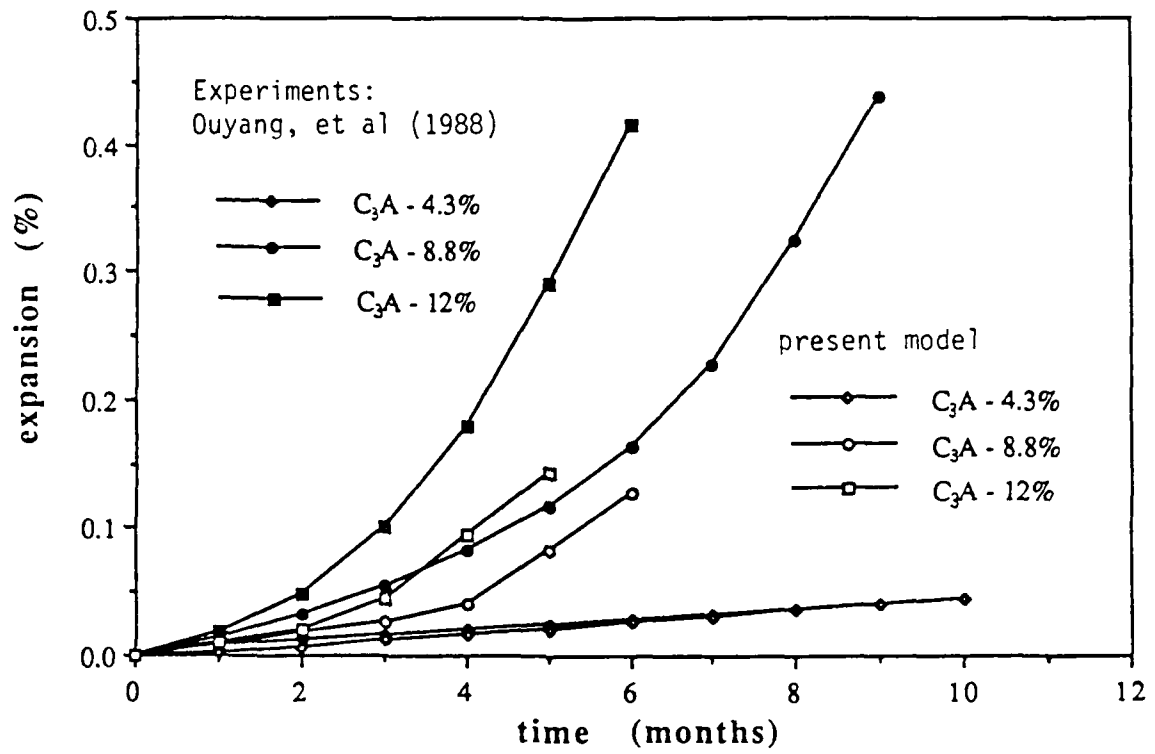FIG.11

STRESS DISTRIBUTION
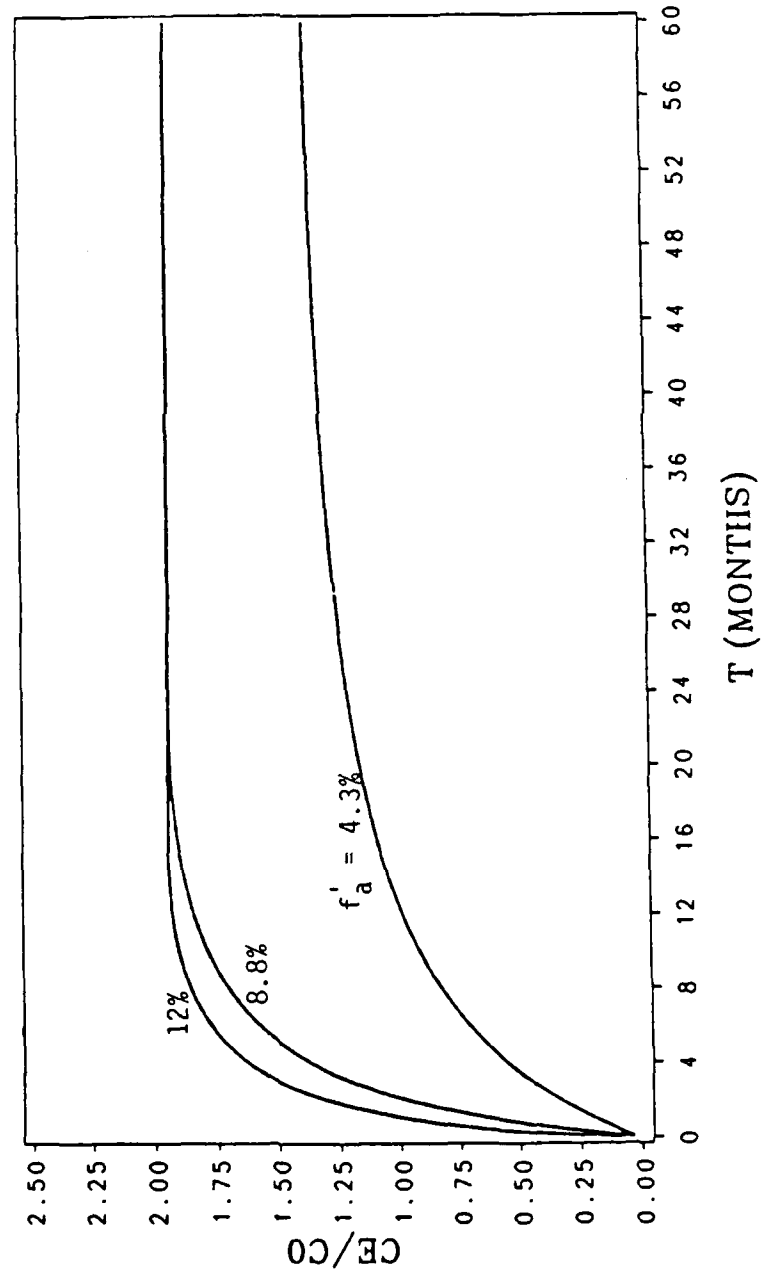
FIG.12

STRESS VARIATION IN CROSS–SECTION

FIG. 13

PROPAGATION OF FRACTURE FRONT

FIG.14

LINEAR EXPANSION OF MORTAR BARS

FIG. 15

ETTRINGITE FORMATION

FIG.16

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APPENDIX A

substance	subscript	molar mass (g/mol)	molar volume (cm³/mol)	density (g/cm³)
$Ca(OH)_2$	c	74.0	33.2	2.23
$MgSO_4$	s	120.4	72.1	1.67
$CaSO_4 \cdot 2H_2O$	g	18.0	18.0	1.00
H_2O	-	172.2	74.1	2.32
$Mg(OH)_2$	-	58.3	24.5	2.38
$3CaO \cdot Al_2O_3$	a	270.2	88.8	3.04
$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$	e	1254.5	725.1	1.73

Table A.1. Molar masses and molar volumes of reacting substances

```
**********************************************************************
*
*    PROGRAM TO SOLVE A PARTIALLY UNCOUPLED SYSTEM OF THE NONLINEAR
*    DIFFUSION EQUATION (7.16) AND THE RATE EQUATION (7.11) FOR THE
*    ETTRINGITE FORMATION, USING THE IMSL ROUTINE (DIVPAG).
*    SINCE THE PROBLEM IS STIFF THE GEAR'S BACKWARD METHOD IS ADOPTED
*
**********************************************************************


         IMPLICIT DOUBLE PRECISION (A-H, O-Z)
         PARAMETER (NEQ=21, NPARAM=50, NSTEP=50, LDA=NEQ)
         DIMENSION A(LDA,NEQ), CE(NEQ), PARAM(NPARAM),YM(NEQ),SIGMA(NEQ)
         EXTERNAL FCN, FCNJ, DIVPAG, DSET, CONST
         COMMON/PASSE/TEND,XX(NEQ),CC(NEQ),DD(NEQ)

                ******* INITIALIZE PARAM - DIVPAG *****

         HINIT = 2.0
         INORM = 1
         METH = 2
         MXSTEP = 2000.
         CALL DSET (NPARAM, 0.0D0, PARAM, 1)
         PARAM(1) = HINIT
         PARAM(4)= MXSTEP
         PARAM(10)= INORM
         PARAM(12) = METH


       ****** INITIALIZE OTHER ARGUMENTS AND INTRODUCE CONSTANTS ******

         CALL DSET(NEQ, 0.0, CE, 1)
         CALL DSET(NEQ,0.0,SIGMA,1)
         CALL DSET(NEQ,0.0,YM,1)
         C =1.0
         W0 = 1.25
         W = W0
         C0 = 0.012
         D0 = 1.0D-8

             ****** 'SRR' IS THE NORMALIZED RATE CONSTANT 'K' ******

         SRR =0.03
         G1 = 0.5D12
         G2 = 0.7D11
         CECR = 1.0/(G2**(1.0/6.0))/C0
         CCR = 1.0

                ****** 'AL' IS THE ADSORPTION CONSTANT 'ALFA' ******
                ****** 'A' IS DETERMINED BY (7.4) AND (7.12) ******
```

```
AL = 0.8
FA = 0.3
PI = CONST('PI')
DELTA=1.0/FLOAT(NEQ-1)
BETA = 0.1
              ****** INITIAL ENTRY ******
IDO = 1

    ****** T IS TIME, TOL - TOLERANCE FOR ERROR CONTROL *****

T = 0.0
TOL = 0.1D-3
TMAX = 300.0
DO 10 K=1, NSTEP
TEND = TMAX*FLOAT(K)/FLOAT(NSTEP)

    ***** INTRODUCE CARSLAW-JAEGER'S SOLUTION (7.17) ******

DZ = D0*24.0*3600.0/(W**2)
DO 20 N=1,NEQ
S = 0.0
X = 1.0-(N-1)*DELTA
XX(N)=X

****** COMPUTE THE DIFFUSIVITY ******

D = DZ*(1.0+G1*(C0*CE(N))**6)
DD(N)=D
DO 30 J=0,500
R = FLOAT(J)
F1 =((-1)**J)/(2.0*R+1.0)*COS(PI*X*(2.0*R+1.0)/2.0)
F2 = EXP(-1.0*D*PI**2/4.0*(2.0*R+1.0)**2*TEND)
S = S+F1*F2
30 CONTINUE
C = 1.0 - (4.0/PI)*S
CC(N)=C
20 CONTINUE

        ****** INTEGRATE 21 ODE (7.11) USING IMSL ******

CALL DIVPAG (IDO, NEQ, FCN, FCNJ, A, T, TEND, TOL, PARAM, CE(1))
WRITE(8,*)'*********************'
WRITE(8,23) TEND,T
23 FORMAT(1X,'TIME = ',F7.1,2X,F7.1)
WRITE(8,*)'*********************'
WRITE(8,77)
77 FORMAT(3X,'X',5X,'C',6X,'CE',7X,'D',7X,'W',6X,'YM',5X,'SIGMA',5X,
&5X,'EX')
```

```
****** CHECK IF THE FRACTURE FRONT APPEARED ******

      DO 66 N=1,NEQ
      IF (CE(N).LT.CECR) THEN
      CONTINUE
      ELSE IF (CE(N+1).LT.CECR) THEN
      CE(N) = CECR
      CE(N+1) = CECR
      CC(N) = CCR
      CC(N+1) = CCR
      NCR=N
      GOTO 15
      ELSE
      CE(N) = CECR
      CC(N) = CCR
      ENDIF
   66 CONTINUE

****** COMPUTE EXPANSION (7.20) OR (7.22) USING SIMPSON'S RULE ****

   15 E1 = 0.0
      E2 = 0.0
      E3 = 0.0
      E4 = 0.0
      DO 11 N=2,NEQ-1,2
      E1 = E1 + CE(N)*(1.0-G2*(C0*CE(N))**6)
      E3 = E3 + 1.0-G2*(C0*CE(N))**6
   11 CONTINUE
      DO 12 N=3,NEQ-2,2
      E2 = E2 + CE(N)*(1.0-G2*(C0*CE(N))**6)
      E4 = E4 + 1.0-G2*(C0*CE(N))**6
   12 CONTINUE
      SM1 =CE(1)*(1.0-G2*(C0*CE(1))**6)+4.0*E1+2.0*E2+
     &CE(21)*(1.0-G2*(C0*CE(21))**6)
      SM2 = 1.0-G2*(C0*CE(1))**6+4.0*E3+2.0*E4+
     &1.0-G2*(C0*CE(21))**6
      EX = BETA*C0*((1.0-W/W0)*CECR+W/W0*SM1/SM2)

****** COMPUTE THE YOUNG'S MODULUS AND AXIAL STRESS ******

      DO 100 N=1,NEQ
      YM(N) = 1.0-G2*(CE(N)*C0)**6
      SIGMA(N) = YM(N)*C0*BETA*(SM1/SM2 - CE(N))
  100 CONTINUE

      DO 21 N=1,NEQ
      WRITE(8,22) XX(N),CC(N),CE(N),DD(N),W,YM(N),SIGMA(N),EX
   22 FORMAT(1X,F4.2,6(F8.5,1X),F9.6)
   21 CONTINUE
```

```
      ****** COMPUTE THE WIDTH REDUCTION ******

   W= W-NCR*W/FLOAT(NEQ-1)
10 CONTINUE

           ****** RELEASE THE WORKSPACE ******
   IDO = 3
   CALL DIVPAG (IDO, NEQ, FCN, FCNJ, A, T, TEND, TOL, PARAM, CE(1))
   END


   ***********************************************************************
   ***********************************************************************


   ****** SUBROUTINE TO EVALUATE THE RIGHT-HAND SIDE OF (7.11) ******

   SUBROUTINE FCN (NEQ, T, CE, CEDER)
   IMPLICIT DOUBLE PRECISION (A-H, O-Z)
   PARAMETER(MEQ=21)
   DIMENSION  CE(MEQ), CEDER(MEQ)
   COMMON/PASSE/TEND,XX(MEQ),CC(MEQ),DD(MEQ)
   SRR = 0.03
   AL = 0.8
   FA = 0.3
   DO 20 I=1,MEQ
   CEDER(I)= SRR*(AL*CC(I)-0.412*CE(I))*(FA-0.215*CE(I))
20 CONTINUE
   RETURN
   END
   ***********************************************************************
   ***********************************************************************


      ****** SUBROUTINE TO COMPUTE THE JACOBIAN ******

   SUBROUTINE FCNJ(NEQ, T, CE, DCDDC)
   IMPLICIT DOUBLE PRECISION (A-H, O-Z)
   INTEGER NEQ
         THIS SUBROUTINE IS NEVER CALLED ; INCLUDED BECAUSE THE
         CALLING SEQUENCE OF DIVPAG REQUIRES IT.
   RETURN
   END
```